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THE ALKALOIDS OF *SENECIO* SPECIES

III. *SENECIO INTEGERRIMUS, S. LONGILOBUS, S. SPARTIOIDES* AND *S. RIDELLII*[1]

BY RICHARD H. F. MANSKE[2]

Abstract

Senecionine is the main alkaloid of *Senecio integerrimus*, but a small amount of a new alkaloid, ***integerrimine*** ($C_{18}H_{25}O_5N$), was also found. *S. longilobus* contains ***longilobine*** ($C_{18}H_{23}O_5N$) and *S. ridellii* contains ***ridelliine*** ($C_{18}H_{23}O_6N$), both alkaloids being new. In addition to the main alkaloid of *S. spartioides*, which was identified as seneciphylline, a minor base, ***spartioidine*** ($C_{18}H_{23}O_5N$), apparently new, was obtained. Hydrolysis of the new alkaloids that were available in sufficient quantity for this purpose yielded, in all cases, retronecine and a new necic acid. A structural formula for senecic acid is proposed.

It has been shown that chemical examination of *Senecio* spp. may be used as an aid to botanical classification.

The chemistry of the alkaloids of *Senecio* species is simplified somewhat by the observation that the basic hydrolytic fragment in most cases consists of retronecine, but it is greatly complicated by the numerous species and by the fact that the acid hydrolytic fragments display an almost bewildering diversity. While there is the strong probability, tantamount to a certainty, that the necic acids are derivatives of terpenes, the presence of two carboxyl and one or more hydroxyl groups, on a carbon skeleton of undetermined nature, does not simplify the rigorous elucidation of structure. It is probable that comparatively large amounts of acids, and therefore alkaloids, will be necessary to solve the structural problems involved, and the investigation described here was initiated with a two-fold end in view. There was the object of finding more convenient sources of known alkaloids, as well as the expectation of finding new ones. In both respects the aims have met with a measure of success.

Senecio integerrimus Nutt. was found to contain two alkaloids. The minor constituent, now termed *integerrimine*, was obtained in only small amounts. It is best represented by $C_{18}H_{25}O_5N$, a formula which is confirmed by the analyses of the fission product. The basic fragment proved to be retronecine. The main constituent was readily obtained in a state of purity. On the basis of analyses, optical rotation, and cleavage products it was definitely

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[1] *Manuscript received December 13, 1938.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

[2] *Chemist, National Research Laboratories, Ottawa.*

characterized as senecionine (1, 2). The alkaloid, *aureine*, which the author isolated from *S. aureus* (6), proved on direct comparison to be identical with senecionine. Furthermore, an alkaloid now isolated from *S. pseudo-arnica* is also senecionine. It is becoming evident that the last-named is one of the most cosmopolitan of *Senecio* alkaloids, Barger and co-workers having found it in at least three species.

The other plants mentioned in the title, namely, *S. longilobus* Benth., *S. spartioides* T. & G., and *S. ridellii* T. & G., are evidently closely related botanically. In the Index Kewensis they are stated to be identical and synonymous with a prior species, namely, *S. douglasii* D.C., but other authorities are not in agreement with this reduction.* *S. douglasii* was not available for chemical examination but the three species cited yielded results which offer a final answer and they are indeed distinct. The main alkaloid which each elaborates differs from those of the other two, although at least two of the alkaloids are derivatives of retronecine.

S. spartioides contains a minor alkaloid, termed *spartioidine*, which, on the basis of analytical data only is probably $C_{18}H_{23}O_5N$. The major base is identical with seneciphylline, an alkaloid isolated by Orekhoff (7) and by Konowalowa and Orekhoff (5) from *S. platyphyllus* and from *S. stenocephallus*, respectively. The author is greatly indebted to Professor Orekhoff and Mme. Konowalowa for carrying out an exact comparison with an authentic specimen.

The alkaloid from *S. longilobus*, $C_{18}H_{23}O_5N$, appears to be new and the name *longilobine* is now proposed for it. Hydrolysis yields retronecine and *longinecic* acid, $C_{10}H_{14}O_5$. In the case of *S. ridellii*, the alkaloid *ridelliine*, $C_{18}H_{23}O_6N$, was not available in sufficient quantity to warrant fission experiments. The minor alkaloid already mentioned, namely, spartioidine, was, for the same reason, not hydrolyzed. It is hoped that more material will be available at a future date.

If it be assumed that senecic acid is a derivative of isoprene, a large number of formulae are possible, but when the known facts are taken into consideration a formula with a great degree of probability can be written. These facts are,— (1) The molecule contains two carboxyl groups; (2) one hydroxyl group which lactonizes readily is present and it is therefore in a γ-position to one of the carboxyls; (3) the hydroxyl group is not likely to be in a γ-position with respect to the second carboxyl since two lactones would then be expected, unless, of course, the two lactones, owing to symmetry, would be identical; (4) one double bond and two or three C-methyl groups are
double bond is present in the group, $CH_3 . CH{=}C<$, since acet
not acetone or formaldehyde (formic acid) is formed in the oxidati

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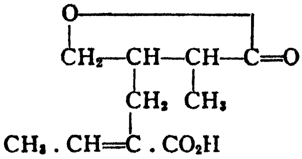
* *The taxonomic difficulties in the genus Senecio are admittedly enormous. Prof. E. D. Merrill, of Harvard University, was consulted, and he intimated that the Kew "reductions" are not entirely reliable and maintained that structural differences alone were sufficient to allocate specific rank to the cases cited. Sir Arthur Hill, Director of the Royal Botanic Garden, Kew, admitted that a re-examination of the material in the Kew Herbarium disclosed specific differences without, however, explaining the original reduction to S. douglasii. The author is greatly indebted to these authorities for their valuable assistance.*

alkaline permanganate. Two formulae which account for the above observations are the following—



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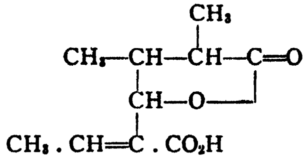
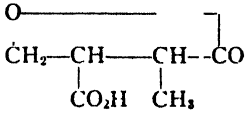


II

The nitric acid oxidation experiments of Barger and Blackie (1) afford the possibility of distinguishing between these formulae. The product which they obtained is a lactone and is best represented by the empirical formula $C_6H_8O_4$. That it is a methyl-paraconic acid of the structure



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is extremely probable, and its formation from a substance of Formula (I) but not from that of Formula (II) is at once obvious. An optically inactive form of such an acid has, in fact, been prepared by Fichter and Rudin (4). It was found to melt at 104° C., whereas that obtained by Barger and Blackie melts at 142° C. These facts, however, do not necessarily prove non-identity. Owing to the presence of two asymmetric carbon atoms, the acid can exist in two racemic and four optically active forms.

Experimental

Senecio integerrimus was collected at Salina Experimental Station, Salina, Utah, in June-July, 1929, and June, 1930. The plant was mature, seed beginning to form. *S longilobus* was collected in Marysvale Canyon, Utah, in September, 1936. The plants were at and past the flower stage. *S. spartioides* was collected at Panguitsh Lake, Utah, in September, 1935, and in August, 1936, the collections thus representing the stages of early flower to fruit formation. *S. ridellii* was collected at Fort Robinson, Nebraska, in August, 1937. These collections were made by field representatives of the U.S. Department of Agriculture and in all cases were identified by their staff of botanists. They were made available for chemical study through the kind collaboration of Dr. J. F. Couch of the Pathological Division of the U.S. Bureau of Animal Industry, and the author takes this opportunity to acknowledge his great indebtedness.

The specimen of *S. pseudo-arnica* was presented to the author by Dr. Jacques Rousseau of the Institute Botanique, Université de Montréal. The specific details for the isolation of *Senecio* alkaloids which the author has outlined in a previous communication (6) have been followed. In all cases ether extraction of the aqueous acid solution, prepared from the total methanol extract, yielded fumaric acid. In a number of cases the addition of ammonia to the acidic solution yielded a crystalline precipitate* which, when sufficiently bulky or sparingly soluble in ether, was filtered off and purified separately.

S. integerrimus

The crystalline precipitate from the basified aqueous solution was washed, dried, and recrystallized to constant melting point from chloroform-methanol. It was obtained in stout colourless elongated plates which melted with decomposition at 237° C.† when placed in a bath preheated to 220° C. In admixture with the author's aureine (6) melting at 235° C. there was no depression in melting point. $[\alpha]_D^{28°} = -51.1°$ ($c = 0.4$ in chloroform). The yield was 0.3%. Found: C, 64.28, 64.40; H, 7.46, 7.55; N, 4.47, 4.43%. Calcd. for $C_{18}H_{25}O_6N$: C, 64.46; H, 7.46; N, 4.18%. These data in themselves are sufficient to warrant the supposition that the alkaloid in question is senecionine. Professor Barger, in a private communication, had previously suggested that *aureine* was probably identical with senecionine.

Further confirmation of this identity was obtained from the products of alkaline hydrolysis. The free base (m.p. 118°) and the hydrochloride (m.p. 164°) proved to be identical with retronecine and its hydrochloride. The acidic fragment, in common with the experience of Barger and Blackie, proved to be difficult to purify. The following procedure has, however, proved reliable and the acid can be obtained in good yield.

The dried crude acid was dissolved in chloroform and the solution slowly evaporated to a small volume. Enough benzene to make a thin syrup was added and the solution seeded with a crystal. At this stage crystallization was slow. When apparently complete, the mixture was filtered and washed with benzene. It was recrystallized twice from chloroform-benzene; it then melted not quite sharply at 150–151° C. One recrystallization, however, from boiling benzene in which it is only sparingly soluble, and which left a small amount of oily residue, yielded well developed individual prisms which melted sharply at 154° C. $[\alpha]_D^{25°} = +38.9°$ ($c = 1.28$ in absolute alcohol). These figures are in satisfactory agreement with those recorded for senecic acid lactone.

The observations of Barger and Blackie on nitric acid oxidation were also successfully repeated with this acid, although the yield of crystalline oxidation product was not satisfactory.

Oxidation of Senecic Acid

The lactone (0.7 gm.) was dissolved in hot water and the solution rapidly cooled. Finely powdered potassium permanganate was added at intervals, the temperature being controlled by cooling in running water. An odour of acetaldehyde became perceptible. Addition of permanganate was continued until the pink colour remained for 30 min. The precipitated manganese dioxide was filtered off, the filtrate acidified with hydrochloric acid, and distilled to a small volume. The distillate gave completely negative tests for acetone and formaldehyde, but yielded a crystalline precipitate when treated with 2 : 4-dinitrophenylhydrazine. The excessively small amount of the phenylhydrazone did not, however, permit further purification. The main portion of the distillate was titrated to neutrality with standard sodium hydroxide solution and evaporated to dryness. The residue was heated under reflux with an alcoholic solution of the calculated quantity of *p*-xenacyl bromide. The resulting ester was purified by recrystallization from methanol and obtained in colourless plates melting at 110° C., either alone or in admixture with an authentic specimen of xenacyl acetate (3).

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* *It is to be observed that this precipitate is contaminated with some inorganic material, the greater portion of which was identified as ammonium magnesium phosphate.*

† *All melting points are corrected.*

Integerrimine

The combined mother liquor, from which no more senecionine could be crystallized, was largely freed of organic solvents, dilute hydrochloric acid added, and the remainder of the organic solvents was boiled off. The filtered solution was repeatedly extracted with ether. Ammonia was then added and the crystalline precipitate filtered off. A further small amount was obtained from the alkaline filtrate by extracting it with ether. The combined base was dissolved in boiling methanol and the somewhat concentrated solution cautiously diluted with water. The crystalline base was filtered off, washed with dilute methanol, and dried. It was then repeatedly extracted with cold ether and the extracts were evaporated to a small volume. The base which then crystallized melted at 171 to 172° C. It was recrystallized from methanol in which it is readily soluble. As thus obtained ***integerrimine*** consists of stout prisms melting sharply and without decomposition at 172 to 172.5° C. $[\alpha]_D^{28°} = +4.3°$ ($c = 0.8$ in methanol). Found: C, 64.41, 64.41; H, 7.54, 7.52; N, 4.35, 4.26%. Calcd. for $C_{18}H_{25}O_5N$: C, 64.46; H, 7.46; N, 4.18%. Hydrolysis of integerrimine with alcoholic alkali yielded retronecine and an acid which, when recrystallized from hot water in which it is readily soluble, consisted of colourless prisms melting at 151° C. It is not identical with senecic acid and, since it is probably a new substance, the provisional name, *integerrinecic* acid, is proposed for it. Found: C, 55.57, 55.38; H, 7.38, 7.38%. Calcd. for $C_{10}H_{16}O_5$: C, 55.56; H, 7.41%.

S. pseudo-arnica

There was available only 1500 gm. of the dried material of this species, from which less than 0.3 gm. of total alkaloid could be isolated. It was recrystallized several times from boiling methanol and obtained in colourless elongated plates melting with decomposition at 237 to 238° C. In admixture with a specimen of senecionine from *S. integerrimus*, there was no observable depression in melting point.

S. longilobus

There was available a total of 5.3 kilos. of the dried plant. The alkaloid ***longilobine*** was recrystallized several times from chloroform-methanol and then consisted of colourless stout prisms melting with decomposition at 217 to 218° C. For this determination it was placed in a bath preheated to 190°C. and sintering was noticeable at 212 to 215° C. The yield was 3.1 gm. $[\alpha]_D^{25°} = -79.2°$ ($c = 2$ in 95% ethanol). Found: C, 64.22, 64.32; H, 7.07, 7.03; N, 4.98, 4.86%. Calcd. for $C_{18}H_{23}O_5N$: C, 64.86; H, 6.91; N, 4.20%.

The *methiodide* was prepared in methanol and recrystallized first by adding acetone to a concentrated aqueous solution, and then from hot methanol in which it is sparingly soluble. The fine prisms thus obtained melted at 249° C. to a dark tar.

Hydrolysis of longilobine yielded retronecine (m.p. 118° C.; hydrochloride, m.p. 164° C.) and an acid which was obtained by ether extraction from the acidified hydrolyzate. The residue from the latter crystallized readily. It was redissolved in dry ether and the filtered solution evaporated to a thin syrup. Petroleum ether (40 to 60°) was added until the incipient turbidity just disappeared on mixing. The addition of a nucleus induced the formation of a hard crust of fine needles in stellate aggregates. *Longinecic* acid as thus obtained melted to a turbid liquid at 126° C. which became clear at 129° C. There was some slight sintering at a lower temperature and at 150° C. a gas, presumably water, indicating lactone formation, was evolved. Found: C, 55.38, 55.48; H, 6.64, 6.72%. Calcd. for $C_{10}H_{14}O_5$: C, 56.08; H, 6.54%.

S. spartioides

A total of 7800 gm. of this plant in the dry condition yielded 42 gm. of crude alkaloid. The greater portion of this crystallized directly when the aqueous acid solution was basified with ammonia. The remainder was recovered from the filtrate by ether extraction. The base was recrystallized from chloroform-methanol and obtained in colourless prisms melting with only slight decomposition at 217° C. In admixture with longilobine it was completely liquid at 215° C. $[\alpha]_D^{23°} = -119.5°$ ($c = 4.0$ in chloroform). Found: C, 64.46, 64.42; H, 6.74, 6.83; N, 4.63, 4 59%. Calcd. for $C_{18}H_{23}O_5N$: C, 64.86; H, 6.91; N, 4.20%.

The above constants are in substantial agreement with those of seneciphylline. Furthermore, hydrolysis yielded retronecine and an acid, recrystallized from ether-hexane, melting at 139° C. Konowalowa and Orekhoff (5) obtained retronecine and an acid melting at 140° to 141° C. from seneciphylline. Madam Konowalowa kindly determined the melting points of seneciphylline, the alkaloid from *S. spartioides*, and a mixture of the two, simultaneously in a bath preheated to 200° C. She observed the following melting points, 212° C., 211° C., and 211° C. (uncorrected) respectively. In addition she prepared the picrates and observed, as before, the respective melting points as 190° C., 189° C., and 190° C. (uncorrected). The alkaloid in question is therefore identical with seneciphylline.

Spartioidine

The mother liquor from which the seneciphylline had been crystallized was evaporated to remove organic solvents and the residue dissolved in dilute acid. The filtered solution was repeatedly extracted with ether, then basified with ammonia, and the resulting crystalline precipitate washed and dried. It was dissolved in hot methanol, and the small amount of seneciphylline which separated on cooling was filtered off. The filtrate on evaporation to a small volume deposited another base which was recrystallized thrice more from hot methanol in which it is moderately soluble. Brilliant stout prisms of *spartioidine* melting sharply and without decomposition at 178° C. were thus obtained (0.1 gm.). Found: C, 64.87, 64.92; H, 6.92, 6.97; N,. 4.74, 4.69%. Calcd. for $C_{18}H_{23}O_5N$: C, 64.86; H, 6.91; N, 4.20%.

The methiodide crystallized directly in colourless fine plates from chloroform–methyl-iodide containing a little methanol. It was washed with the latter solvent and it then melted with decomposition at 239° C.

S. ridellii

The yield of recrystallized base from 120 gm. of material was 0.8 gm. The once-recrystallized substance melted at 196° C. without appreciable decomposition, and further recrystallization did not alter this value. *Ridelline* forms stout well developed prisms sparingly soluble in methanol. Found: C, 61.90, 61.90; H, 6.75; 6.73; N, 4.38, 4.35%. Calcd. for $C_{18}H_{23}O_6N$: C, 61.89; H, 6.59; N, 4.01%.

The *methiodide* prepared in methanol–methyl-iodide crystallized with great facility. It was recrystallized from hot water (sparingly soluble in the cold) and washed with methanol in which it is virtually insoluble; it then melted to a dark tar at 250° C., some darkening taking place at 240° to 245° C.

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THE ALKALOIDS OF *SENECIO* SPECIES

IV. *ERECHTITES HIERACIFOLIA* (L.) RAF.[1]

BY RICHARD H. F. MANSKE[2]

Abstract

An examination of *Erechtites hieracifolia* (L.) Raf., during which two alkaloids have been isolated, has emphasized the close chemical relation which the genus *Erechtites* bears to *Senecio*. The chief alkaloid, *hieracifoline*, $C_{18}H_{25}O_5N$, on hydrolysis yields retronecine and *hieracinecic* acid. The alkaloid is therefore of the type generally elaborated by *Senecio* species.

Hitherto the genus *Senecio* was the only one in the Compositae Family whose species were known to contain well authenticated alkaloids. The genus *Erechtites* Raf. is closely related taxonomically to *Senecio* and both genera are included in the tribe Senecioneae. It therefore seemed of interest to examine a species of *Erechtites* in order to determine whether the taxonomic similarity had its parallel in alkaloid constituents.

E. hieracifolia (L.) Raf., frequently called the fireweed but entirely distinct from *Epilobium* which is also known by the same common name, is cosmopolitan in eastern North America. A preliminary examination revealed the presence of bases, and although the content is extremely low, it has been possible to isolate two alkaloids in a state of purity. The chief of these is one for which the name *hieracifoline* is proposed. Analytical figures require $C_{18}H_{25}O_5N$, and this observation alone is sufficient to indicate the close relationship to the *Senecio* alkaloids with some of which hieracifoline is isomeric but apparently not identical. Nevertheless the similarity is still further indicated by the nature of the hydrolytic products. The basic fragment proved to be identical with retronecine. The acid, hieracinecic acid, is evidently dibasic.

The second alkaloid is also definitely of the *Senecio* type. The author has for some time made use of Ehrlich's reagent as a diagnosis for *Senecio* alkaloids. They generally melt with decomposition or decompose when heated to 200° to 220° C. The resulting melt gives a positive test for the pyrrole nucleus, an indication that a hydro- or hydroxy-pyrrole is present in the parent base. This test, when applied to the *Erechtites* base melting at 237° C.,* is strongly positive.

Experimental

Hieracifoline

The isolation of the total bases was effected by the procedure recorded in a previous communication (1), namely,— extraction with methanol, extraction of the extract with dilute hydrochloric acid, exhaustion of the filtered aqueous solution with ether**, and finally extraction of the alkaloids from the basified solution with ether.

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[1] *Manuscript received December 13, 1938.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa.

[2] *Chemist, National Research Laboratories, Ottawa.*

* *All melting points are corrected.*

** *This ether extract, as in all Senecio spp., yielded an appreciable quantity of fumaric acid.*

The crude alkaloid from *Erechtites hieracifolia* was recrystallized several times from chloroform-methanol and *hieracifoline* was then obtained in large colourless plates melting at 227° C. in a yield of 0.016%. $[\alpha]_D^{26°} = -89.7°$ ($c = 0.4$ in chloroform). Found: C, 64.49, 64.39; H, 7.25, 7.01; N, 4.40, 4.62%. Calcd. for $C_{18}H_{25}O_6N$: C, 64.47; H, 7.46; N, 4.18%.

Hydrolysis of Hieracifoline

A suspension of the base (0.9 gm.) in methanolic potassium hydroxide was boiled until it had dissolved. The methanol was evaporated from the solution, 0.5 cc. water added, and the remainder of the methanol evaporated. The cooled paste was repeatedly extracted with ether and the combined extract evaporated to a small volume. Spontaneous crystallization of the characteristic elongated plates of retronecine occurred almost at once. After filtering and washing with a little ether, the dried base melted sharply at 119° C., either alone or in admixture with an authentic specimen of retronecine. The yield was 0.3 gm.

The alkaline paste from which the retronecine had been extracted was acidified with hydrochloric acid and extracted again with ether. The residue from the ether extract was treated with a little benzene and warmed gently. The acid which readily crystallized was filtered off and redissolved in a large volume of boiling benzene in which it is only sparingly soluble. The filtered solution was evaporated to a small volume and the crystals which separated on cooling were filtered off and washed. As thus obtained the crystals were not well developed. A product of better appearance was obtained when the acid was dissolved in dry ether, in which it is readily soluble, and the solution evaporated to a thin syrup. The addition of benzene yielded *hieracinecic* acid in stellate aggregates of fine needles which, when washed with benzene and dried, melted sharply at 132° C. The melt solidified on slight cooling and then remelted at 131 to 132° C. Found: C, 55.87, 55.84; H, 7.09, 7.08%. Calcd. for $C_{10}H_{16}O_5$: C, 55.56; H, 7.41%.

The Minor Alkaloid

The combined mother liquor from the crystallization of hieracifoline was evaporated to a resin and the latter dissolved in dilute hydrochloric acid. The filtered solution was exhausted with ether, basified with ammonia, and the liberated bases were extracted with ether. The washed extract was evaporated to a small volume and treated with a little methanol. The crystals which had separated in the course of several days were filtered off and recrystallized several times from chloroform-methanol. The *base* then consisted of hard stout prisms, with pointed terminations, which melt with decomposition at 237° C. Senecionine (2) melts at the same temperature but a mixture of the two was liquid at 216 to 220° C. The yield was about 0.003%. Found: C, 65.04, 65.00; H, 4.77, 4.65; N, 3.72, 3.82%. Calcd. for $C_{20}H_{19}O_6N$: C, 65.04; H, 5.15; N, 3.79%. Calcd. for $C_{20}H_{17}O_6N$: C, 65.39; H, 4.63; N, 3.81%.

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2. Manske, R. H. F. Can. J. Research, B, 17 : 1-7. 1939.

SYNTHESIS OF NAPHTHYL-ACETIC ACID[1]

By A. Cambron[2]

Abstract

A simple and convenient method* for the preparation of α-naphthyl-acetic acid from readily obtainable starting materials is described.

A convenient method for the preparation of α-naphthyl-acetic acid has become of particular interest since Zimmerman and Wilcoxon (16) reported that this acid possessed properties similar to those of indole-acetic as a plant growth promoter or for initiating root formation.

Boessneck (4), who was the first to synthesize α-naphthyl-acetic acid, obtained it by the following procedure:

$$\alpha C_{10}H_7COCl \longrightarrow C_{10}H_7COCN \longrightarrow C_{10}H_7COCONH_2 \longrightarrow C_{10}H_7COCOOH \longrightarrow \alpha C_{10}H_7CH_2COOH\,.$$

Other methods of synthesis were later reported by Tiffeneau and Daudel (14, p. 679), who used the Grignard reaction between 1-bromo-naphthalene and acetaldehyde; by Weitzenböck and Lieb (15, p. 556), who prepared the intermediate α-naphthyl-acetamide by the action of ammonium sulphide on methyl-α-naphthyl ketone; and by several other chemists, who followed various procedures (2, p. 205; 8,9).

The first simple method reported in the literature is that described by Mayer and Oppenheimer (11, p. 2139) and later used by Zimmerman and Wilcoxon (16) and by Olivier and Wit (12). This method consists in brominating α-methyl-naphthalene at a temperature of 200° C., and converting the bromo-methyl-naphthalene to the nitrile, which is then hydrolyzed to the acid:

$$C_{10}H_7CH_3 \longrightarrow C_{10}H_7CH_2Br \longrightarrow C_{10}H_7CH_2CN \longrightarrow C_{10}H_7CH_2COOH\,.$$

Attempts to duplicate the experiments of Mayer and Oppenheimer (11, p. 2139) did not at first yield satisfactory results. This was later found to be due to the fact that the bromination was being carried out in the dark in an enclosed electrically heated air bath. The original authors very probably operated in a vessel exposed to direct or diffused sunlight. Their method was considerably improved by carrying out the reaction in a Pyrex flask irradiated by a carbon arc, the yield of bromide obtained under these conditions being 59% of the theory as compared to a yield of 43.5% reported by them. This observation was confirmed in a report published shortly afterwards by Olivier and Wit (12), who carried out the same reaction in quartz glass irradiated by a mercury lamp. These authors, however, reported a yield of bromide of only 32%.

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[1] *Manuscript received December 22, 1938.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

[2] *Chemist, National Research Laboratories, Ottawa.*

* *Patents applied for.*

The above method suffers from a serious disadvantage in that α-methyl-naphthalene is a costly material, and, furthermore, is difficult to obtain free from the β-isomer. Consequently, an alternative method for the production of the required halogen-substituted α-methyl-naphthalene was investigated. This method is based on a reaction first observed by Grassi and Maselli (7), who reported the formation of benzyl chloride by the action of *s*-dichloromethyl ether, formed by the action of hydrochloric acid on formaldehyde, on benzene. Blanc (3) used the same reaction for the preparation of chloromethyl-naphthalene and reported a yield of 54% based on the naphthalene used, but Anderson and Short (1), who followed Blanc's procedure, obtained a yield of only 11%. By modification of Blanc's procedure, however, the yield was raised to 42%.

A modification of the above method for the preparation of chloromethyl-naphthalene is described in D.R.P. 533,132. The method was later used by Rupe and Brentano (13), and by Coles and Dodds (5). The procedure described in the above patent consists in treating a mixture of naphthalene, 30% formaldehyde, and concentrated hydrochloric acid with concentrated sulphuric acid at 60° C., the sulphuric acid being added in the course of a few hours and the reaction mixture being then kept at 60°, with good stirring for about 20 hr.

A further modification of the same method was described by Darzens and Lévy (6). Their method consists in adding an excess of gaseous hydrochloric acid to a suspension of paraform in glacial acetic, then reacting the solution of *s*-dichloromethyl ether thus formed with an equimolecular proportion of naphthalene, no condensing agent being used. Their procedure requires a heating period of 20 hr. They claimed a yield of 71.5%, based on naphthalene. An attempt to duplicate their experiment did not confirm this claim, the highest yield obtained being 31.6%. It was found, however, that by the use of essentially the same procedure as that described by these authors, the yield of chloride could be increased to 45% by using phosphoric acid as a condensing agent, and, further, that under these conditions the time of reaction was reduced to about 10 hr. The time required for completing the reaction was further reduced by using aqueous concentrated hydrochloric and by increasing the temperature from 60° to 98°–100° C. The yield of chloride under these conditions is 56.5% of theory, based on the total naphthalene used, and 67% based on naphthalene reacted, the reaction being completed in 4½ hr.

The second step in the synthesis of α-naphthyl-acetic acid, when the starting material is chloro- or bromo-methyl-naphthalene, is the conversion of the halogen compound to the corresponding nitrile. This is effected by the known method of refluxing the halogen compound with an alcoholic solution of potassium cyanide.

The third and final step in the synthesis is the hydrolysis of the nitrile. Mayer and Oppenheimer (11, p. 2139) describe a method for the hydrolysis of α-naphthyl-acetonitrile by refluxing with potassium hydroxide in the presence of hydrogen peroxide. The same method has been used by Olivier and Wit (12) who found, however, that the presence of the peroxide was not only superfluous but diminished the yield. The latter authors report that attempts to effect the hydrolysis of the nitrile by the action of phosphoric acid were unsuccessful, owing to the decomposing action of the acid on the product.

The present author has found that the hydrolysis of the nitrile by the action of alkalis, whether carried out with or without the addition of hydrogen peroxide, yields a product extremely difficult to purify, several recrystallizations being required before it is obtained in a satisfactory state of purity. It was found, however, that the hydrolysis could be carried out more conveniently and a more easily purified product obtained by effecting the hydrolysis with a mixture of equal volumes of sulphuric acid, acetic acid, and water.

R. H. F. Manske and A. E. Ledingham, of these laboratories, have done further work on the present synthesis of naphthyl-acetic acid, particularly with the object of identifying the by-products formed in the various stages of the synthesis (10).

Experimental

α-Chloromethyl-naphthalene

A mixture of paraform (90 gm.), naphthalene (288 gm.), acetic acid (250 gm.) concentrated hydrochloric acid (280 cc.), and syrupy phosphoric acid (135 cc.) was heated at 98 to 100° C. for 4½ hr. with good stirring. The reaction mixture was then poured into two litres of cold water, the product being obtained in the form of an oil heavier than water. The product was washed by stirring two or three times with two litres of water, and decanting the aqueous layer. The oil was then filtered from a small amount of an insoluble by-product and distilled under reduced pressure. Yields: 223 gm. of a product boiling at 145° to 160° C. at 6 to 8 mm.; 56.5%, based on naphthalene used.

α-Naphthyl-acetic acid

The chloromethyl compound was first converted to the nitrile. α-Chloromethyl-naphthalene (223 gm.) was refluxed for an hour with a solution of potassium cyanide (110 gm.) in ethyl alcohol (500 cc.) and water (200 cc.). The alcohol was distilled off, the product washed with water, filtered from water insoluble solids, dried under reduced pressure, and distilled, the fraction boiling at 175 to 185° at 11 to 14 mm. being collected.

The acetonitrile was hydrolyzed by refluxing with a mixture of sulphuric acid (350 cc.), acetic acid, (350 cc.), and water (350 cc.), at 120 to 125° for 45 min. The crude acid was then precipitated by pouring the reaction mixture in three litres of cold water with good stirring. The acid was purified by dissolving in 50% alcohol, treating the boiling solution with charcoal, and precipitating the acid by dilution with cold water; yield, 131.5 gm. of α-naphthyl-acetic melting at 131.5°. This represents an over-all yield of 31.5%, based on the naphthalene used.

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A SYNTHESIS OF α-NAPHTHYL-ACETIC ACID AND SOME HOMOLOGUES[1]

By Richard H. F. Manske[2] and Archie E. Ledingham[3]

Abstract

In the course of a study of the synthesis of α-naphthyl-acetic acid, a method was elaborated by Dr. A. Cambron that made available large quantities of α-chloromethyl-naphthalene. During the purification of the crude product and in the later stages of the synthesis we have encountered a number of by-products. Among others, these include methyl α-naphthyl-methyl ether, di-α-naphthyl-methyl ether, α-naphthyl carbinol, and 1 : 5-bis-chloromethyl-naphthalene. The last-named was converted into 1 : 5-naphthylene-diacetic acid, m.p. 280° C., via the corresponding nitrile. δ-(1-Naphthyl)-valeric acid, m.p. 84° C., and ε-(1-naphthyl)-hexoic acid, m.p. 62° C., were synthesized by standard procedures.

The observation of Zimmerman and Wilcoxon (12), that α-naphthyl-acetic acid possesses properties similar to those of indolyl-3-acetic acid in initiating certain responses in plants, has aroused some interest in its further chemical study as well as in procedures designed to render it readily accessible (4, 9, 11).

The obvious starting material is α-chloromethyl- or α-bromomethyl-naphthalene. The subsequent stages involving the preparation and hydrolysis of the corresponding cyanide would not be expected to offer serious difficulties. While the bromination of α-methyl-naphthalene, particularly in the light of a mercury vapour lamp, proceeds moderately well (8), some nuclear bromination is certain to occur, and the elimination of the halogen from the final product is difficult.

A number of procedures for the preparation of α-chloromethyl-naphthalene from naphthalene, formaldehyde, and hydrogen chloride have been published recently (1, 2). The reaction involved is an extension of that used by Stephen, Short, and Gladding (10) and involves only a change of condensing agents and modified temperatures. Dr. A. Cambron (see preceding paper), of these laboratories, has made a study of this condensation, and the crude α-chloro-methyl-naphthalene which he has obtained was kindly placed at our disposal for further study. On careful fractionation it yielded a product which consisted very largely of the α-isomer, although we have reason to believe that a small amount of the β-isomer is present and prevented the complete crystallization of our purest distillate. A higher boiling fraction consisted of a readily crystallizable mixture from which apparently-pure 1 : 5-bis-chloromethyl-naphthalene has been obtained. Anderson and Short (1) have established the orientation of this compound, and our observations fully confirm theirs. Admixed with the crude product are probably isomeric bis-chloromethyl-naphthalenes as well as a small amount of α-naphthyl-carbinol. The latter

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presumably arises from the hydrolysis of the chloride. It was isolated in the course of purification of the dicyano-compound prepared from the dichloro-compound. The former was hydrolyzed to naphthylene-1 : 5-diacetic acid. The orientation of this acid was established by conversion to 1 : 5-dimethyl-naphthalene by heating the potassium salt with soda-lime.

A number of by-products were encountered when the α-chloromethyl-naphthalene was converted to α-naphthyl-acetic acid. The nitrile was accompanied by a somewhat more volatile non-nitrogenous liquid which proved to be methyl-α-naphthyl-methyl ether. The higher boiling fraction contained some α-naphthyl-acetamide and di-α-naphthyl-methyl ether. Both of the ethers are regarded as the result of the action of the alkali contained in the cyanide on the chloride, and the methyl ether owes its presence to the use of methanol as solvent. It is a liquid which yields a well crystallized picrate, whereas the symmetrical ether is a crystalline solid.

Hydrolysis of the nitrile in alkaline solution is rather slow. Hydrolysis with sulphuric acid in slightly diluted acetic acid yields an acid contaminated with some of the amide and a neutral nitrogenous substance, the nature of which is still obscure. Analytical figures indicate $C_{24}H_{21}ON$ or a lower homologue, but in either case the hydrogen content is too large to be accounted for by condensation and elimination reactions alone.

We have prepared a homologous series of ω-(1-naphthyl)-aliphatic acids up to and including ε-(1-naphthyl)-hexoic acid, in order to observe their effect on plant growth. Dr. N H. Grace has this problem under study and will report upon it shortly. It may be mentioned, however, that all members of the series show some activity as phytohormones.

The propionic and butyric acids were prepared by published methods, and for the synthesis of the valeric and hexoic acids we condensed the appropriate ω-(1-naphthyl)-alkyl bromides with sodio-malonic ester. The bromides were obtained from the corresponding alcohols and these in turn were prepared by the Bouveault reduction For practical purposes these syntheses reach their limit in the hexoic acid, the salts of which possess the properties of soaps. With the higher homologues the yields in the malonic ester synthesis are materially reduced, and the alcohols are convertible into bromides only with difficulty. Even the crystallization of the final products is by no means facile, and the melting points (61° C. for the hexoic acid) fall rapidly with increase in chain length.

Experimental

α-Chloromethyl-naphthalene

The crude α-chloromethyl-naphthalene obtained from Dr. Cambron was fractionated *in vacuo*; it yielded a forerun of unchanged naphthalene and then the main fraction of the chloro-compound distilling at 148 to 150° C. (14 mm.). It finally crystallized for the greater part, and the isolated crystals melted sharply at 32° C.* There was present a small amount of oil which could not be separated by distillation alone, but it, too, solidified completely on cooling to 0° C. It is probable that the liquid is a mixture containing a small amount of β-chloromethyl-naphthalene.

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* *All melting points are corrected.*

1 : 5-Bis-chloromethyl-naphthalene

The high boiling residue from the fractionation of the α-chloro-compound crystallized for the greater part on cooling. It was transferred to a short necked flask, and the fraction boiling at 175 to 185° (12 mm.) collected separately. The distillate was recrystallized twice from hot benzene and was obtained in colourless prisms melting at 144° C. Calcd. for $C_{12}H_{10}Cl_2$: C, 64.02; H, 4.45; Cl, 31.53%. Found: C, 64.42; H, 4.58; Cl, 31.47%.

Naphthylene-1 : 5-diacetonitrile†

A solution of crude 1 : 5-bis-chloromethyl-naphthalene (85 gm.) in 150 cc. of dioxane was added to potassium cyanide (55 gm.) in 50 cc. of water, and the mixture heated on the steam bath for 24 hr. The resulting dicyano-compound was isolated by extracting the diluted mixture with benzene. The benzene solution was filtered to remove some suspended material and washed with dilute acid and with water. Removal of the benzene yielded an oil which was distilled under reduced pressure. The low boiling fraction (up to 200° C. at 2 mm.) yielded some α-naphthyl-carbinol (*vide infra*). The main fraction, b.p. 200 to 235° (2 mm.) mostly at 230° C. (2 mm.), crystallized readily. It was washed once with methanol and redissolved in chloroform-acetone. The somewhat concentrated solution yielded, on the addition of methanol, colourless fine needles of naphthylene-1 : 5-diacetonitrile melting at 140° C. Calcd. for $C_{14}H_{10}N_2$: C, 81.55; H, 4.85; N, 13 59%. Found: C, 81.50; H, 5.06; N, 13.46%.

Naphthylene-1 : 5-diacetic Acid

A mixture of naphthylene-1 : 5-diacetonitrile (5 gm.), sulphuric acid (21 gm.), acetic acid (24 gm.), and water (8 cc.) was heated in a flask fitted with a stirrer. After 5 to 10 min. at 100° to 110° C. the heterogeneous mixture became clear and in about 45 min. crystals began to separate. After one hour the mixture was diluted with water, and the sand coloured crystals were filtered off and washed. The acid was purified by solution in alkali and reprecipitation with acid and finally by recrystallization from hot methanol in which it is sparingly soluble. As thus obtained naphthylene-1 : 5-diacetic acid consists of fine colourless needles melting at 280° C. Calcd. for $C_{14}H_{12}O_4$: C, 68.85; H, 4.92%; Equiv. 244. Found: C, 68.84; H, 5.11%; Equiv. 246.

A small amount of the crude acid was decarboxylated by heating the potassium salt with soda-lime in a stream of nitrogen. The distillate was collected in ether and the washed and filtered solution evaporated. The residual oil was converted to a picrate in methanol solution and recrystallized from hot methanol. The stout bright orange prisms thus obtained melted at 138° C.; this is the melting point recorded for the picrate of 1 : 5-dimethyl-naphthalene (1).

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† *In conformity with the term phenylene for the disubstituted benzene derivatives, the term* naphthylene *is used for the disubstitution products of naphthalene.*

α-Naphthyl-carbinol

The low boiling fraction from the preparation of the dinitrile on extended hydrolysis with methanolic potassium hydroxide yielded some naphthylene-1 : 5-diacetic acid and a neutral oil which was extracted from the alkaline solution with benzene. It was distilled *in vacuo* and the main fraction, b.p. 143 to 145° (2 mm.), which solidified on cooling was recrystallized from benzene-hexane. The colourless needles thus obtained melted at 64° C. and in admixture with a specimen of α-naphthyl-carbinol, prepared as described below, there was no depression in melting point. Calcd. for $C_{11}H_{10}O$: C, 83.54; H, 6.33%. Found: C, 83.49; H, 6.58%.

The carbinol in question was prepared from α-chloromethyl-naphthalene as follows: a solution of the latter (35 gm.) and potassium acetate (25 gm.) in acetic acid (70 gm.) was heated under reflux for two hours. Benzene was added and the mixture washed with water. Evaporation of the benzene and distillation of the residue yielded *α-naphthyl-carbinyl acetate* as a colourless thin oil boiling at 134 to 136° (1.5 mm.). This was hydrolyzed with alcoholic potassium hydroxide and the unsaponifiable oil extracted with benzene. The benzene was removed *in vacuo* and the residue distilled. The fraction boiling at 140 to 143° (1.5 mm.) crystallized immediately when inoculated with a specimen of α-naphthyl-carbinol obtained as described above. Two recrystallizations from benzene-hexane yielded colourless needles melting at 63° C. The over-all yield was 80 to 90% of the theoretical.

α-Naphthyl-acetonitrile

A mixture of sodium cyanide (80 gm.), water (100 cc.), α-chloromethyl-naphthalene (205 gm.), and methanol (400 cc.) was heated under reflux for one hour. The cooled mixture was diluted with water and extracted with benzene The residue, after the removal of the solvent, was distilled and the fraction boiling at 140 to 160° (1 mm.) collected. The yield was uniformly 180 gm.

Large quantities of the crude nitrile were redistilled through a long column, and the pure nitrile was obtained as a colourless oil boiling at 150 to 152°C. (1.5 mm.) in yields approximating 85%.

Methyl α-Naphthyl-methyl Ether

The low boiling fraction from the preparation of α-naphthyl-acetonitrile was refractionated several times and ultimately obtained as a colourless oil boiling at 101 to 103° C. (1.5 mm.). Analyses indicate that this substance is methyl α-naphthyl-methyl ether. Calcd. for $C_{12}H_{12}O$: C, 83.71; H, 6.98%. Found: C, 83.69; H, 7.00%.

The *picrate* was recrystallized from methanol and obtained in yellow needles melting at 95° C. Calcd. for $C_{22}H_{21}O_7N$: N, 10.47%. Found: N, 10.37%.

Di-α-naphthyl-methyl Ether and α-Naphthyl-acetamide

The high boiling fraction from the preparation of α-naphthyl-acetonitrile was obtained as a pale yellow oil boiling at 175 to 185° C. (1.5 mm.). This in contact with acetone-methanol yielded a copious crop of crystals. The product was redissolved in chloroform-methanol and the filtered solution evaporated to a small volume. Crystallization followed the addition of methanol and the substance (m.p. 118° C.), when recrystallized again from chloroform-methanol, was obtained in uniform stout parallelepipeds, the angles approaching 90°, melting sharply at 121° C. Analyses prove this substance to be *di-α-naphthyl-methyl ether*. Calcd. for $C_{22}H_{18}O$: C, 88.59; H, 6.04%. Found: C, 88.55; H, 6.17%.

The filtrate from the first recrystallization of the above-described ether was evaporated to a small volume and cooled. The crystalline product which separated was recrystallized twice from hot methanol, and obtained in long stout prisms melting at 184° C. Recrystallization from much hot water did not change the melting point. It contains nitrogen and undoubtedly consists of α-naphthyl-acetamide which has been described by Bössneck (3) as melting at 180 to 181° C. (? corr.).

α-Naphthyl-acetic Acid

α-Naphthyl-acetonitrile is conveniently hydrolyzed by the following procedure, the essential features of which were suggested to us by Dr. Cambron. A mixture of the nitrile (70 gm.), sulphuric acid (150 gm.), water (54 cc.) and acetic acid (100 cc.) in a long necked flask is stirred and slowly heated to 110 to 115° C., at which temperature a mild exothermal reaction sets in and a homogeneous solution results. Stirring with heating just to the boiling point is continued for one hour, during which the mixture becomes heterogeneous again. A little water is added and the whole is poured into a large volume of water with vigorous stirring. The filtered, washed, and dried product is obtained in a yield of 95 to 98% of the theoretical. Preliminary purification can be effected by dissolving in aqueous ammonia and reprecipitating with acid.

A neutral nitrogenous substance, insoluble in ammonia, was encountered at this point. It was partly purified by heating with alcoholic potassium hydroxide, during which process some ammonia was evolved. It is probable that the latter resulted from the hydrolysis of some α-naphthyl-acetamide, since the corresponding acid could be obtained from the alkaline solution. The insoluble residue was recrystallized twice from chloroform-methanol, once from dioxane-acetone, and finally from dioxane in which it is moderately soluble only when hot. The fine, apparently homogeneous, needles thus obtained melted at 179° C. The substance contains nitrogen, and analyses indicate the formula $C_{23}H_{19}ON$ or $C_{24}H_{21}ON$. Oxidation with chromic acid in acetic acid yielded no definite product. Found: C, 84.30, 84.15; H, 5.97, 5.98; N, 3.98, 4.13%. Calcd. for $C_{24}H_{21}ON$: C, 84.96; H, 6.19; N, 4.13%.

Complete purification of α-naphthyl-acetic acid is conveniently effected by partial precipitation from an alkaline solution, the first small portion being rejected. Subsequent recrystallization from water and then from benzene yields the acid in dense stout prisms melting at 134° C. When this product is recrystallized again from water it melts at 132° C., presumably owing to the occlusion of small amounts of water.

The methyl ester boils at 168 to 170° (2 mm.).

δ-(1-Naphthyl)-valeric Acid

The β-(1-naphthyl)-propionic acid required for the synthesis of the valeric acid was prepared from α-chloromethyl-naphthalene and sodio-malonic ester. It possesses the properties recorded by Meyer and Sieglitz (6). The methyl ester melts at 36° C. and is the only crystalline ester which has been encountered in the homologues of α-naphthyl-acetic acid. It boils at 145° (1 mm.).

Reduction of the ester with sodium and alcohol (5) yielded γ-(1-naphthyl)-propanol as a faintly yellow oil boiling at 145° (1 mm.) in 70% of the theoretical. This was converted into the bromide in a yield of 70 to 75% by the following procedure, which was also used to convert β-(1-naphthyl)-ethanol and δ-(1-naphthyl)-butanol into the corresponding bromides.

The alcohol was alternately saturated with gaseous hydrogen bromide and heated on a steam bath, until the necessary increase in weight was obtained. Toward the end of the reaction a few drops of sulphuric acid may be added to advantage. The mixture was diluted with benzene and washed with sulphuric acid until the acid layer was virtually colourless. The benzene solution was then washed with 10% sodium chloride solution, and the solvent finally distilled. The residue was distilled *in vacuo* and 3-(1-naphthyl)-1-bromopropane obtained as a colourless oil boiling at 153 to 155° (3 mm.).

Condensation of the bromide with sodio-malonic ester was effected in boiling absolute ethanol and the substituted malonic ester isolated by extracting with benzene and washing with water. In this case, as in those concerned with the synthesis of the butyric and hexoic acids, distillation of the malonic ester was unsatisfactory, owing to the large amount of unsaponifiable high boiling resin formed during the malonic ester condensation. The solvent was therefore removed and the residue hydrolyzed with alcoholic potassium hydroxide. The alcohol was boiled out of the diluted solution, and the aqueous solution extracted with benzene to remove resin. It was filtered and acidified with hydrochloric acid. The oily malonic acid derivative crystallized eventually. It was filtered off, decarboxylated at 190 to 200° C. and the cooled melt recrystallized from benzene and then from benzene-hexane. Fine colourless needles of δ-(1-naphthyl)-valeric acid melting at 89° C. were obtained in a yield of 20 to 25% based on the bromide taken. Calcd. for $C_{15}H_{16}O_2$: C, 78.95; H, 7.02%. Found: C, 77.75; H, 8.53%. The methyl ester, b.p. 153 to 155° (3 mm.), was obtained only as an oil.

ε-(1-Naphthyl)-hexoic Acid

β-(1-Naphthyl)-ethanol was converted into the bromide, by the procedure outlined above, which was obtained in a yield of 73% of the theoretical. It boils at 135 to 138° (1.5 mm.). Its purity was checked by a bromine analysis. (Calcd. for $C_{12}H_{11}Br$: Br, 34.0%. Found: Br, 33.4%). Condensation with sodio-malonic ester, leading ultimately to the synthesis of γ-(1-naphthyl)-butyric acid, was carried out by the procedure recorded by Schlenk, Bergmann, and Bergmann (8). The acid was obtained from benzene in elongated plates melting at 112° C. in an over-all yield of 58% based on the bromide used.

The methyl ester is an oil boiling at 152 to 155° (0.5 mm.).

Reduction of the methyl ester of γ-(1-naphthyl)-butyric acid in absolute ethanol with sodium (5) gave an 83% yield of δ-(1-naphthyl)-butanol as a colourless oil boiling at 150 to 155° (0.5 mm.). The bromide was obtained from it as a colourless oil boiling at 160 to 163° (2 mm.) in a yield of 39% of the theoretical.

The conversion of the 4-(1-naphthyl)-1-bromobutane into ε-(1-naphthyl)-hexoic acid was effected as in the case of the lower homologue. The corresponding malonic acid did not crystallize and several weeks elapsed before a crystal nucleus of the mono-basic acid was obtained. It was then possible to recrystallize it from hexane in which it is moderately soluble. The purified acid melts at 62° C. and consists of small colourless prisms. The yield, based on the bromide, was 20 to 25%. Calcd. for $C_{16}H_{18}O_2$: C, 79.34; H, 7.44%. Found: C, 77.98; H, 8.82%.

An aqueous alkaline solution of the acid exhibits a slight opalescence and foams like a soap solution.

Acknowledgment

The authors record their indebtedness to Mr. C. W. Davis of these laboratories for carrying out a number of analyses.

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THE OCCURRENCE OF *l*-NICOTINE IN *ASCLEPIAS SYRIACA* L.[1]

BY LÉO MARION[2]

Abstract

The root of *Asclepias syriaca* L., contains an alkaloid which has been identified as *l*-nicotine. The base was characterized via its picrate and picrolonate.

The Australian plant *Duboisia hopwoodii,* belonging to the natural family Solanaceae, is the only well established source of *l*-nicotine (3) which has been found extraneous to the *Nicotiana* spp. Preobraschensky (2) claimed to have found nicotine in *Cannabis sativa,* a plant belonging to the family Urticaceae. Some doubt has been cast on this work by Siebold and Bradbury (4), who re-examined the plant and obtained a basic oil apparently different from nicotine. They assigned the name cannabinine to this base, although they did not characterize it further. The occurrence of *l*-nicotine in *Asclepias syriaca* L., a milkweed of widespread distribution, is now placed on record. This plant belongs to the Asclepiadaceae. Owing to the presence of nicotine in *A. syriaca,* a plant which is quite remote from the *Nicotiana* spp., it would seem that the claim of Preobraschensky should not be too lightly dismissed, and that it could be discredited only after a rigorous investigation of *Cannabis sativa.*

The root of *Asclepias syriaca* L., was found to contain a small quantity (0.001%) of an oily base which could be distilled to a colourless oil having a strong odour of nicotine. It was characterized by means of its picrate and its picrolonate, the melting points of which were determined before and after admixture with the corresponding compounds prepared from an authentic specimen of *l*-nicotine.

Besides *l*-nicotine, the methanolic extract of the plant was found to contain fumaric acid and a substance, m.p. 190° C.*, which yielded analytical figures in good agreement with $C_{16}H_{26}O$. This substance may be identical with *Asclepion,* isolated in an impure condition by List (1) from the milky sap of the plant.

Experimental

The roots of *Asclepias syriaca* L. (23 kilos), collected in the neighbourhood of Ottawa, were dried, ground and extracted in Soxhlets with methanol. The solvent was largely distilled from the extract, and the residue heated on the steam bath with water slightly acidified with acetic acid. After the insoluble material had been filtered off, the filtrate was basified with potassium hydroxide and distilled in steam under reduced pressure. The distillate was acidified with a little hydrochloric acid, concentrated under reduced pressure

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* *All melting points are corrected.*

to about 500 cc., filtered, and strongly basified with saturated aqueous potassium hydroxide. The basic solution was extracted repeatedly with ether and the combined ethereal extracts were distilled on the steam bath to remove the solvent. A dark brown oil was left.

Isolation of l-Nicotine

The dark brown basic oil was distilled *in vacuo* and an oil collected which was redistilled at 85° (1 mm.). Wt., 0.21 gm. (yield, 0.001%). About one-half of the oil was converted to a picrate which was recrystallized from boiling methanol as yellow needles, m.p. 228°. Calcd. for $C_{22}H_{20}O_{14}N_8$: C, 42.58; H, 3.22; N, 18.06%. Found: C, 42 79; H, 3.25; N, 17.97%. Admixture with an authentic specimen of *l*-nicotine dipicrate (m.p. 228°) did not depress the melting point. The remainder of the oil was dissolved in aqueous acetone and treated with the calculated quantity of picrolonic acid. The crystalline picrolonate, after recrystallization from boiling acetone, melted at 228°, either before or after admixture with authentic *l*-nicotine dipicrolonate.

Isolation of Fumaric Acid

Some of the aqueous solution which had been steam distilled was acidified with hydrochloric acid and extracted with ether. The ethereal extract yielded an acid which, after several recrystallizations from water, melted at 295°. Admixture with fumaric acid failed to lower the melting point.

Isolation of a Neutral Substance

When the root was extracted in a percolator with cold methanol, and the extract slightly concentrated *in vacuo*, a crystalline substance was gradually deposited from the cooled methanolic solution. This substance was purified by several recrystallizations from a mixture of ethyl acetate and methanol. The colourless crystals, which were deposited in stellar aggregates, melted at 190° C. Calcd for $C_{16}H_{26}O$: C, 82.01; H, 11.11%. Found: C, 82.10, 82 00; H, 11.13, 11.16%.

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VAPOUR-PHASE CRACKING OF GAS-OIL IN BAFFLED METAL TUBES[1]

By Adrien Cambron[2] and Colin H. Bayley[2]

Abstract

The vapour phase cracking of a gas-oil fraction has been investigated under conditions of turbulent and streamline vapour flow. The results show that the increased rate of heat transfer and the more uniform temperature distribution brought about by turbulence cause a very marked increase in the amount of low boiling liquids and olefines produced at the lower temperatures, particularly in the range 600 to 700° C. The character of the vapour flow was also found to have a marked influence on the composition of the liquid products, there being considerably more aromatics produced, especially at the higher temperatures, under conditions of highly turbulent flow.

At 600 and 650° C., for instance, 8 4 and 16 1% of the gas-oil put through was recovered as 205° end-point gasoline when an empty tube was used. However, when a baffled tube was employed, the yield of 205° end-point gasoline was 16 0 and 22 4% respectively, under the same conditions of temperature and liquid rates.

At 800° C. about 23% of the gas-oil put through was recovered as 205° end-point gasoline when either the empty or the baffled tube was used. In the latter experiments, however, 40% of the gasoline consisted of benzene and 20% of toluene, while in the former, the gasoline contained only about 15% of benzene and 5% of toluene.

Experiments have been carried out in which a fraction of the off-gas was recirculated, with the entering gas-oil vapours, through the cracking furnace. Such a procedure did not increase the yield of gasoline, and apparently decreased the yield of aromatics.

The vapour-phase cracking of heavy petroleum fractions first became of technical interest during the Great War (9, 11) when attempts were made to utilize the process for the production of aromatics, particularly toluene. It has been stated (5), however, that the complexity of the products obtained by a process such as Hall's, for instance, rendered the isolation of the lower aromatics commercially impractical, especially when toluene could be extracted in large quantities from Borneo petroleum.

Although a considerable amount of work has been done on the subject of vapour-phase cracking, the results of only a few investigations have been published. Geniesse and Reuter (6, 7) determined the relation between temperature and rate of cracking of gas-oil, and showed that long times of contact at low temperatures gave essentially the same amount of cracking as short times of contact at high temperatures. These authors also determined the independent effect of the time and temperature factors on the yield and the composition of the gasoline and of the fixed gases produced. The highest temperature used by the above-mentioned authors was 700° C. Groll (8) investigated the vapour-phase cracking of gas-oil and of other heavy fractions over a wider temperature range, using temperatures up to 850° C. Groll used

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Note: *The work described in this paper was carried out in 1934.*

metal reaction tubes, and most of his experiments were carried out in the presence of steam. His results confirmed Geniesse and Reuter's conclusions that the composition and the yield of the products are functions of temperature and time of contact, and an attempt was made to determine the nature of this function in the case of a given charging stock.

A growing demand for high antiknock fuels, resulting from the use of increasing compression ratios by the automobile industry, has in the last few years caused a revival of interest in the vapour-phase cracking of heavy hydrocarbons. Several difficulties, however, have retarded the development of vapour-phase processes. Of these difficulties the most important are: (i) the high olefine content of the cracked distillate, which causes considerable losses on refining; (ii) the hydrocarbon loss due to the formation of fixed gases; and (iii) the low rates of throughput as compared with liquid-phase processes, this being due primarily to the fact that the rate of heat transfer from heating surface to vapour is considerably lower than the rate of heat transfer to a liquid.

The first of the above difficulties has been largely overcome by the use of special activated clays for the refining of the raw vapour-phase distillates. By the use of these clays the reactive gum-forming di-olefines are removed, whereas the mono-olefines are not, and appear as valuable antiknock constituents in the refined distillate.

With regard to the formation of fixed gases in vapour-phase processes, an apparently successful attempt has been made to reduce the losses due to gas formation by polymerizing the olefines present in these gases to liquids, and it is stated that improvements in the vapour-phase process, together with the increased gasoline yields due to the polymerization operation, now permit this process to compete favorably with the liquid-phase cracking process (10). Besides their possible use for the production of gasoline, vapour-phase cracking gases, which contain a high concentration of the lower olefines, are becoming increasingly important as a raw material for the production of industrial organic chemicals.

It has been shown (1, 3) that the pyrolysis of gaseous paraffins can be carried out at considerably higher space velocities under conditions of highly turbulent gas flow, as induced by the use of specially designed baffles, owing to the marked increase in the rate of heat transfer from tube wall to gas under these conditions. As a further consequence of the use of baffled tubes, the liquid products obtained under conditions of highly turbulent flow are much less complex than the products obtained when the pyrolysis of the lower paraffins is carried out under normal flow conditions, the more uniform temperature distribution in the reaction zone under the former conditions tending to suppress side reactions. The object of the present investigation was primarily to determine whether the vapour-phase cracking of heavy petroleum fractions in baffled tubes would lead to the same effects, that is, whether higher vapour rates could be used and less complex products obtained when the reaction is carried out under conditions of highly turbulent flow.

Materials

The experiments described below were carried out with two samples of gas-oil and one of kerosene obtained from Imperial Oil Ltd. These samples were marked respectively *A*, *B*, and *C*. The specific gravity, aniline point, and A.S.T.M. distillation data of each sample are given in Table I.

Experiments 396 and 398 were carried out with gas-oil *A*; Experiment 402 with sample *C*; all other experiments were carried out with sample *B*.

TABLE I
PROPERTIES OF CHARGING STOCKS USED

Sample	*A*	*B*	*C*
Sp. gr. at 25°C.	0 853	0 855	0 803
Aniline point	63 0	62 2	—
A.S.T.M. distillation, %	Temperature, °C.		
(1st drop)	213	215	189
10	232	233	205
20	239	240	209
30	245 5	245	213.5
40	253	251	217
50	263	260	223
60	274	270	228
70	289	284	233.5
80	308	300	241
90	338	337 5	252.5
End	373	—	272

Apparatus

All experiments were carried out with a 28% chromium alloy reaction tube (Allegheny 55) having an internal diameter of 2.5 cm. and a heated length of 145 cm.

In Experiments 406 to 410 no baffles were used. All other experiments were carried out in a tube fitted with baffles consisting of circular discs, 2.25 cm. in diameter, cut from 0.37 mm. sheet, supported 1.6 cm. apart on a 0.65 cm. rod that extended

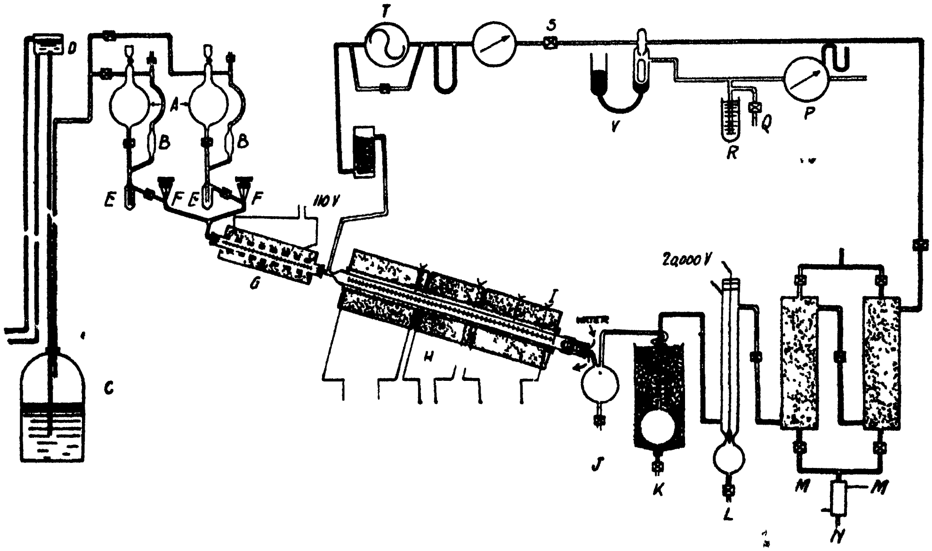

FIG. 1. *Apparatus used in vapour-phase cracking of gas-oil.*

throughout the heated length of the tube. The baffles and support were of the same material as the tube.

A diagram of the apparatus is given in Fig. 1.

The furnace was heated by means of nichrome windings wound in sections and well insulated, the current supplied to each section being independently controlled. Temperatures were determined by means of thermocouples, *I*, placed in the air space between the winding and the tube, the distance between the winding and the tube wall being about 1 in.

The volume of the reaction space was 690 cc.; this includes the volume of the first 30 cm. section which was kept at a lower temperature and was used as a vaporizer and preheater.

The liquid feed was controlled as follows: About 800 gm. of oil was put in one of the reservoirs, *A*, the liquid being kept under the air pressure corresponding to a 7 ft. head of water between the constant level tank, *D*, and the bottle, *C*. (The other reservoir, *A*, was used for other experiments in which large quantities of liquid were put through the furnace, the arrangement shown permitting recharging without interrupting the experiment.) It was found that under these conditions the control of the liquid rate through the graduated needle valve, *F*, was independent of any slight variation in the back pressure from the furnace. The rate of flow could be checked in the course of an experiment by closing the valve under the reservoir, and determining the time required by the liquid to run past the graduations on the small calibrated bulb, *B*. The trap, *E*, was put in to catch any solid particles and prevent stoppage of the needle valve. The liquid was partly vaporized in the electrically heated tube, *G*. This consisted of a 2.0 cm. quartz tube, 38 cm. long, the heat being supplied by means of a well insulated winding. The maximum current that could be supplied to this tube was insufficient to vaporize the oil completely at the high liquid rates used, and the first 30 cm. section of the cracking furnace was kept at 650° C. to complete vaporization and preheat the vapours. The vapours and gases from the furnace were cooled by means of a water cooled copper spiral before emerging from the tube. Some of the vapours condensed in *J* and in the ice cooled condenser, *K*, and the tar-fog carried over was precipitated in the Cottrell, *L*, the condensable vapours being removed from the gas by the charcoal absorbers, *M*. The residual gas passed through the valve, *V*, and past the trap, *R*, and the meter, *P*, to waste, samples being taken at *Q* during each experiment.

In the last series of experiments a fraction of the off-gas was recirculated through the furnace by means of the pump, *T*, the valve *S* being opened. The amount of gas recirculated was controlled through the valve, *V*. The rest of the gas was allowed to escape through the meter, *P*, as before.

Experimental

Single Pass Cracking Experiments

A few preliminary experiments were made with gas-oil *A* and kerosene *C*, a baffled tube being used. The data given in Table II are typical of the results obtained in these experiments. In the same table are given the results obtained in the experiments carried out under carefully controlled conditions, gas-oil *B* (Experiments 406 to 415) being used. The composition of the gases obtained in the above experiments is given in Table III.

TABLE II

Gasoline yields in baffled and unbaffled tubes

No.	Oil sample	+ or − baffles	Oil charged		Temperature, °C.		Liquid products,		205° end-point gasoline	
			Total	Rate, gm./hr.	1st section	2nd section	Total, gm.	Per cent yield, based on oil put through	Per cent of total liquid	Per cent yield, based on oil put through
396	*A*	+	819.0	2240	535	645	458	56.0	37	20.7
398	*A*	+	750.5	2145	565	710	367.7	49.0	47	23.0
402	*C*	+	716.3	2390	630	782	265.0	37.0	60	22.2
406	*B*	−	763.8	2035	595	600	678.0	88.8	9.5	8.4
407	*B*	−	765.5	2090	585	650	649.0	84.8	19	16.1
408	*B*	−	762.0	2080	520	700	559.6	73.5	26	19.1
409	*B*	−	748.0	2090	595	750	463.5	62.0	36	22.3
410	*B*	−	759.5	2068	670	800	403.0	52.9	45	23.9
411	*B*	+	755.1	2210	550	600	636.4	84.3	19	16.0
412	*B*	+	755.8	2110	590	650	544.9	72.1	31	22.4
413	*B*	+	752.8	2100	610	700	408.0	54.2	45	24.4
414	*B*	+	768.2	2142	600	750	336.0	43.7*	46	20.1*
415	*B*	+	816.5	2225	630	800	363.6	44.5	50	22.3

[1] *Some of the liquid from the charcoal absorbers was lost.*

TABLE III

Composition of gaseous products

No.	Total gas, litres	Litres/hr.	Composition (% by volume)							Total olefines produced, gm.		Per cent yield olefines, based on oil put through
			C_2H_2	C_2H_4	C_3H_6	C_4H_8	H_2	Residue		C_2H_4	C_3H_6	
								%	C_n*			
396	89.7	245	0.0	35.1	2.1	0.0	10.4	52.4	1.14	–	–	–
398	264.5	757	2.6	20.9	25.3	3.3	10.5	37.4	1.00	69.1	125.5	25.9
402	314.6	1050	1.3	28.0	18.4	1.0	12.4	38.9	1.07	110.1	108.5	30.5
406	34.1	91	0.1	20.8	20.9	1.7	7.7	43.4	1.27	8.9	13.4	2.9
407	72.3	197	0.3	21.4	25.2	0.9	9.3	40.9	1.22	19.3	34.2	7.0
408	182.0	361	0.5	19.8	27.1	3.8	9.7	37.5	1.08	32.7	67.0	13.1
409	205.0	560	0.4	21.5	24.6	2.8	11.5	38.1	1.12	55.1	94.5	20.0
410	283.0	770	0.6	22.4	22.8	0.4	12.9	39.9	1.06	79.2	121.0	26.3
411	69.1	173	0.0	18.3	29.9	2.8	8.2	39.6	1.21	15.8	38.7	7.2
412	124.3	347	0.6	19.2	28.8	4.2	9.2	37.7	1.23	29.8	67.1	12.8
413	233.0	650	0.6	20.4	26.6	3.2	9.8	38.6	1.09	59.4	116.4	23.4
414	325.8	908	1.0	21.7	19.8	5.8	11.8	39.0	1.08	88.4	121.0	27.2
415	370.0	1010	0.5	24.4	12.6	1.1	16.5	44.4	1.01	112.8	87.4	24.5

* *Carbon number of residue.*

The results of the preliminary experiments, Nos. 396, 398, 402, showed that the optimum temperature for the vapour-phase cracking of the petroleum fractions used was below 800° at rates of about 2000 gm. per hour. As this was well within the temperature range at which the furnace could be operated and as the liquid recovery apparatus was found adequate for collecting the liquids in the off-gas, the above rate was adopted in subsequent experiments.

As already stated, the conditions under which Experiments 406 to 415 were carried out were carefully controlled in order to determine the effect of induced turbulence, particularly on the amount of cracking at a given temperature, and on the nature of the liquids produced. In the first five of the above-mentioned experiments no baffles were used; in the last five, baffles were used.

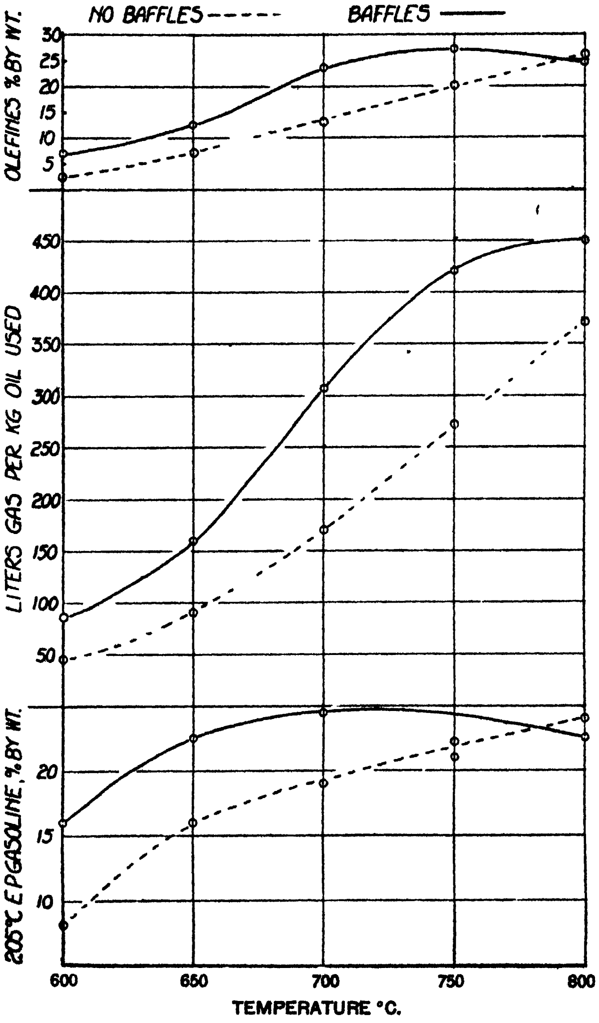

FIG. 2. *Effect of baffles on yield of gasoline and gaseous products.*

Yield of 205° C. End-point Gasoline

The yields of 205° end-point gasoline obtained on one passage in the baffled and in the unbaffled tube respectively have been plotted in Fig. 2. Curves showing the amounts of gas produced and the yields of olefines under the two conditions have been plotted in the same figure. It will be observed that under otherwise identical conditions as to temperature and gas-oil rate, the amount of cracking, as shown by the yield of low boiling products and of olefines, is almost double in the temperature range 600 to 700° when baffles are used. It will also be observed that the yield of 205° end-point gasoline is about the same at 650° C. in the baffled tube as at 750° C. in the open tube. The difference in the amount of cracking under the two conditions is obviously due to the considerably higher rate of heat transfer from tube wall to vapour in the baffled tube, in spite of the fact that the vapour velocity in the open reaction tube was undoubtedly in the critical range at which turbulence appears. The foregoing results confirm the data previously obtained in experiments on the pyrolysis of hydrocarbon gases (1, 2, 3, 4). In fact, the efficiency of the particular design of baffles used in producing a high degree of turbulence, and consequently a high rate of heat transfer, appears to be markedly greater in the case of the heavy petroleum vapours than with hydrocarbon gases.

It is interesting to compare the results obtained at 800° C. by the use of a baffled tube with the results obtained by Groll (8) at the same temperature by the use of an open tube. In Experiments 1 to 10 (8, p. 790), for instance, Groll obtained a conversion of gas-oil to 205° end-point gasoline of 18.5% at 800° C. The composition of this gasoline, as shown by its distillation curve, is very similar to that of the low boiling products obtained at the same temperature in our Experiment 427 in a baffled tube, but the yield of gasoline in the latter experiment was 22 3% of the gas-oil charged. The striking difference between the two experiments, however, lies in the rates of throughput under the two conditions. In Groll's experiment, the gas-oil was put through at the rate of 1.32 litres per litre of reaction space per hr., while in our experiments the corresponding rate was 3.77 litres per litre per hr., an increase of almost 200%. Although the observed temperature was the same in both cases, it may be pointed out that the temperature in Groll's experiments was recorded by means of a thermocouple placed along the axis of the reaction tube, while in our experiments, in which electrical heating was used, the thermocouples were placed in the air space between the heating elements and reaction tube. Hence it is probable that the temperature recorded under our conditions was appreciably higher than that which would have been recorded by thermocouples placed inside the reaction tube.

In Groll's experiment it was found necessary to introduce a small amount of steam along with the oil vapours, in order to suppress carbon formation. We found the addition of steam unnecessary, the deposition of carbon being negligible in the experiments with baffles, this being due in part to the high vapour rates used, but mostly to the more even temperature distribution throughout the reaction chamber and the decrease in the thickness of the stationary gas film on the heating surface resulting from turbulence.

The boiling range and densities of these fractions show that the heavy residues obtained below 700° C. without baffles and below 650° C. with baffles contain a large proportion of unchanged paraffins. In Experiment 412, for instance, in which the yield of gasoline was 22.4% on one passage, the heavy residue represented 50% of the oil put through, and from the distillation range of this material and its specific gravity one would expect an appreciable increase in the yield of gasoline on recycling. It would appear that the optimum temperature under the conditions studied would be between 600 and 650° C., with recycling, if maximum production of aromatics is not desired. The specific gravity of the fractions obtained at temperatures higher than 750° C. indicates the presence of increasing amounts of aromatics. The composition of these fractions was not investigated any further, and the amounts obtained were insufficient to permit the carrying out of recycling experiments.

Recirculation Experiments

A series of experiments was carried out to determine the effect of recirculating a fraction of the off-gas with the oil vapours through the cracking furnace. This was done in an attempt to improve the vapour flow conditions in the cracking tube, and to increase, if possible, the yield of aromatics by polymerizing some of the olefines present in the off-gas. A baffled tube was used in all experiments.

The results obtained are recorded in Tables V and VI.

TABLE V

YIELD OF 205° END-POINT GASOLINE IN RECIRCULATION EXPERIMENTS

No.	Oil put through		Off-gas	Temperature °C		Liquid products		205° End-point gasoline	
	Total, gm	Rate gm /hr	Recycling rate, litres/hr.	1st section	2nd section	Total gm	Per cent yield based on oil put through	Per cent of total liquid	Per cent yield based on oil put through
428	724	1057	251	650	800	342 6	47 3	47 0	22 2
429	741	1060	224	650	750	355 7	47 9	47 7	22 9
430	731	1060	220	650	700	370 0	50 7	41 7	21 1
431	680	1360	216	655	800	317 8	46 7	45 3	21 2
432	750	2050	248	660	800	346 6	46 2	46 1	21 3
433	750	2140	245	680	750	406 5	54 1	38 7	21 0
434	750	2140	221	660	700	496 7	66 1	30 8	20 4

It will be observed that recirculation did not improve the yield of 205° end-point gasoline based on oil put through, even at low liquid rates, and resulted in an appreciable decrease in the percentage of benzene and toluene in the low boiling products obtained at 750° and 800° C. The latter result was unexpected, as it was believed that the formation of aromatics would be favoured by increasing the time of contact of the gases containing a high

TABLE VI

COMPOSITION OF GASES OBTAINED IN RECIRCULATION EXPERIMENTS

No.	Gas produced		Composition						Total olefines produced, gm.		Per cent yield olefines based on oil put through
	Litres /hr.	Total gas, litres	C_2H_2	C_2H_4	C_3H_6	H_2	Residue %	Residue C_n	C_2H_4, gm.	C_3H_6, gm.	
428	468	316	1 0	22 7	10 6	15 7	50 0	1 0	89 7	63 0	21 5
429	450	315	0 8	17 6	18 2	13 8	49 6	1 0	69 3	107 8	23 9
430	331	228	1 0	20 4	14 1	–	–	–	–	–	–
431	627	314	1 0	22 9	10 9	14 2	51 0	1 0	89 8	64 3	21 1
432	895	328	1 2	19 7	20 9	9 7	49 1	1 0	80 7	129 0	30 8
433	617	216	1 3	20 7	26 8	10 4	50 8	1 06	55 9	109 0	22 0
434	376	132	1 3	18 6	28 7	9 2	42 2	1 05	30 6	71 1	13 6

concentration of olefines. The distillation curves of the products obtained in the above-mentioned experiments, Fig. 5, also show that the low boiling fractions, in particular those obtained at 750° and 800° C., are more complex than

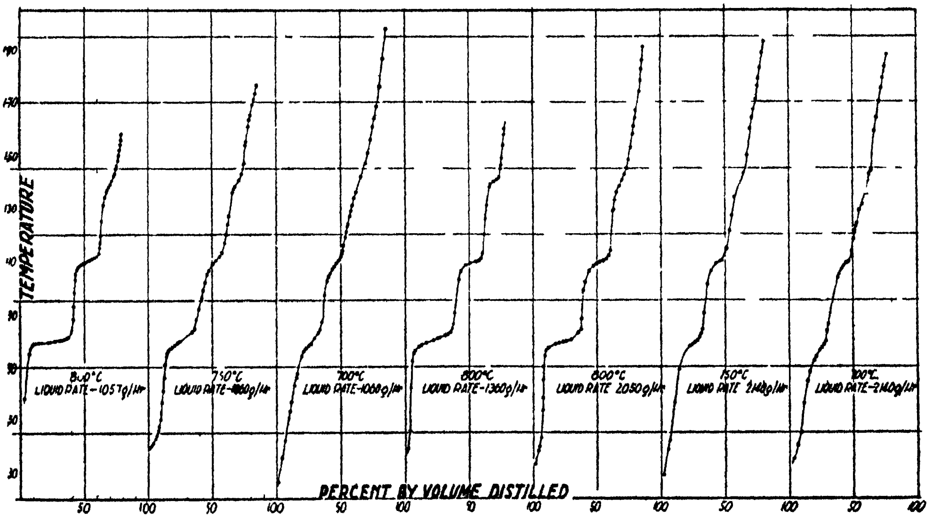

FIG. 5. *Fractional distillation curves for light oils obtained at various temperatures in recycle experiments in baffled tubes.*

the corresponding fractions from single pass cracking experiments. On the other hand, the A.S.T.M. distillation data and specific gravity of the heavy residues, that is, of that fraction of the liquid products boiling above 205° C., show that the heavy residues from experiments carried out with recirculation contain less aromatics or other condensed products than the corresponding fractions from single pass cracking experiments, and consequently would probably give higher yields of gasoline on recycling.

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THE INFLUENCE OF TEMPERATURE ON THE SORPTION OF SODIUM HYDROXIDE ON WOOD[1]

By G. R. Lusby[2] and O. Maass[3]

Abstract

The sorption of sodium hydroxide on black spruce has been measured at 20°, 50°, and 75° C., and was found not to change very much between 20° and 75°. An increase in temperature causes the break in the sorption curve to occur at a higher concentration of alkali. Cooking action begins between 50° and 75°, and tends to obscure the effect of an increase in temperature above 50°.

Introduction

In the alkali-cooking of wood, sorption must play a part, and for the interpretation of the mechanism of cooking, data regarding the influence of temperature and concentration changes on the amount of sorption must be made available. Richardson and Maass (10) made measurements of the sorption of sodium hydroxide on white spruce wood at room temperature. In the present work it was considered of interest to carry out similar measurements on a different species of wood, and to attempt to measure the sorption existing at temperatures approaching the range in which cooking takes place. Since the sorption data are to be used for elucidating the mechanism of cooking, the mechanism of sorption itself should be determined first.

Cotton has been used as the source of cellulose in virtually all researches on alkali sorption recorded in the literature, little work having been done on wood. For reviews of the extensive literature relating to alkali sorption the reader is referred to papers by Clibbens (3), Blanco (2), and Schwarzkopf (12).

When any form of cellulose is placed in a solution of sodium hydroxide, the concentration of the latter decreases rapidly and reaches a constant value within a short time. The explanation of this phenomenon is that sodium hydroxide has been taken up by the cellulose. Since cellulose has a strong affinity for water, it is certain that water also must be taken up by the cellulose in the alkaline solution. The observed decrease in concentration then represents the net effect of the sorption of sodium hydroxide and water by the cellulose. For this reason Neale (7, 8, 9) describes this phenomenon as a "preferential absorption" of sodium hydroxide. Richardson and Maass (10) use the term "pseudo sorption" with the same meaning, since in the calculation of the alkali taken up by the cellulose, the water taken up is neglected. The extent to which this value differs from the true quantity of sodium hydroxide taken up by cellulose depends to a large extent on the amount of water taken

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up. The simple general term "sorption" will be used in this discussion with the meaning of "alkali preferentially taken up" by wood or cellulose.

Vieweg (13) found that when the amount of sodium hydroxide sorbed by cotton is plotted against concentration of alkali, a sharp rise in the curve is noted at a concentration of 3 to 4 molar. The curve then flattens out and becomes horizontal. At a concentration of about 9 molar, another rise, or "break", in the curve occurs. Vieweg (14) repeated this work in 1924 and obtained a slightly different curve. Other workers have obtained similar results. In Fig. 1 the dotted line represents data obtained by Heuser and Bartunek (5). Rumbold (11) obtained a sorption curve with a flat part in the concentration range 1.0 to 1.9 molar. Richardson and Maass (10), as a result of accurate sorption measurements at high concentrations of sodium hydroxide, showed that there is another flat part in the sorption curve besides the parts observed by Vieweg, Rumbold and others. A curve indicating flat parts was also found in the case of white spruce by Richardson and Maass (10), and the breaks in both curves, *i.e*, for cellulose and for wood, occurred at the same concentrations of alkali.

Few sorption measurements have been made at temperatures other than room temperature. D'Ans and Jäger (4) determined the sorption of sodium hydroxide on pulp and cotton at 2° C., and Beadle and Stevens (1) obtained isothermals between 5° and 40°. The results obtained by these writers show that an increase in temperature decreases the amount of sorption and increases the concentration at which the break in the curve occurs.

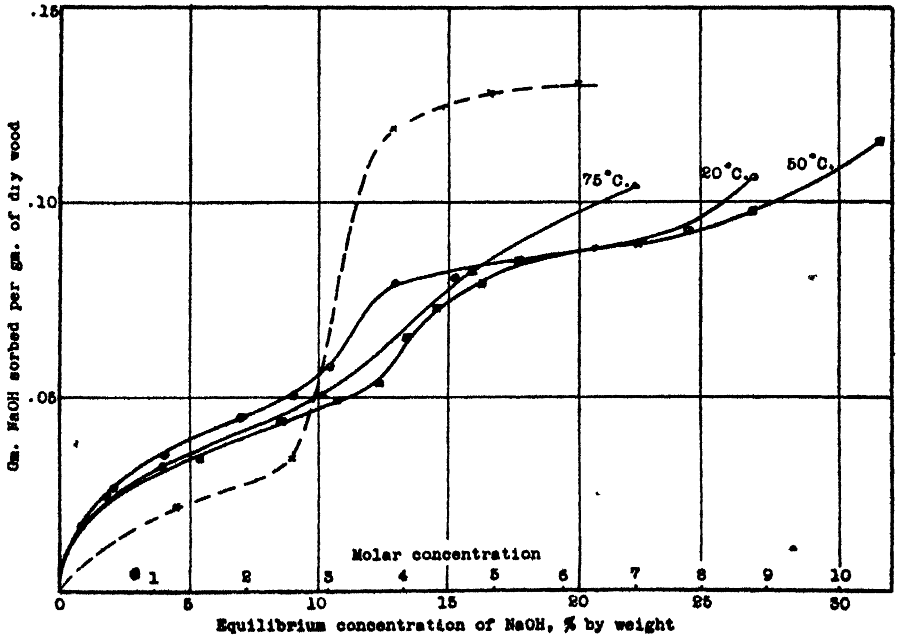

FIG. 1. *Sorption of sodium hydroxide on black spruce in one hour.*

TABLE I

SORPTION OF SODIUM HYDROXIDE ON BLACK SPRUCE AT 20° C.

Equilibrium concentration, molar	Sorption, gm. per gm. of wood	Equilibrium, concentration, molar	Sorption, gm. per gm. of wood
1.030	0.035	7.640	0.089
1.069	.036	7.790	.096
2.808	.058	8.690	.107
2.873	.058	8.750	.104
3.623	.080	11.25	.153
3.755	.079	11.51	.109
4.453	.078	11.53	.096
4.520	.080	13.03	.099
6.380	.088	13.28	.082
6.425	.085	—	—

TABLE II

SORPTION OF SODIUM HYDROXIDE ON BLACK SPRUCE AT 50° C.

Equilibrium concentration, molar	Sorption, gm. per gm. of wood	Equilibrium concentration, molar	Sorption, gm. per gm. of wood
0.2308	0.0172	3.735	0.043
0.2345	.0193	3.803	.063
0.2448	.0186	3.870	.068
0.2510	.0170	4.075	.073
0.4918	.0202	4.083	.072
0.4975	.0244	4.768	.076
0.5020	.0247	4.820	.081
0.5113	.0142	5.260	.093
0.5120	.0252	5.306	.075
1.133	.0335	5.315	.080
1.440	.0339	5.321	.090
1.445	.0340	6.965	.090
2.315	.0430	7.010	.089
2.325	.0376	8.655	.096
2.943	.048	8.655	.098
3.000	.051	10.60	.122
3.483	.054	10.61	.117
3.500	.053	14.70	.159
3.653	.059	14.90	.112
3.685	.048	14.93	.140
3.703	.056	—	—

TABLE III

SORPTION OF SODIUM HYDROXIDE ON BLACK SPRUCE AT 75° C.

Equilibrium concentration, molar	Sorption, gm. per gm. of wood	Equilibrium concentration, molar	Sorption, gm. per gm. of wood
1.047	0.0320	6.925	0.103
1.093	.0342	6.975	.105
2.783	.049	9.010	.129
2.900	.051	9.145	.085
4.650	.082	12.09	.135
4.683	.082	12.13	.108

Experimental Procedure

For details of experimental procedure, the reader is referred to the paper by Richardson and Maass (10), who made determinations at room temperature; in the present work, measurements have been made at temperatures as high as 75° C. Slight modifications were introduced to eliminate errors brought about by the higher vapour pressure of water at 75°. The accuracy was similar to that obtained by Richardson and Maass. Instead of white spruce, black spruce was used, and the samples were prepared in the manner described by Richardson and Maass. The weight of sample used in an experiment varied from 1.8 to 3.8 gm. and the volume of solution was 8 to 10 ml. per gm. of wood. All calculations were based on the oven-dry weight of wood.

Experimental Results

The data obtained are given in Tables I, II, and III, and are presented in the form of isothermals in Fig. 1.

Discussion

The 20° isothermal is quite similar to that obtained by Richardson and Maass (10) for white spruce. The 50° isothermal shows that the effect of an increase in temperature is to cause the break in the curve to occur at a higher concentration of alkali. It would be expected that the break in the 75° isothermal should lie to the right of that in the 50° isothermal, but actually most of the sorption values at 75° are intermediate between the 20° and 50° values.

The high sorption values at 75° appear to be due to the cooking action which takes place at that temperature. This was indicated by the results of experiments in which wood was placed in sodium hydroxide solution and the concentration determined at various times. At 20° the change in concentration was found to be complete within one hour. At 50° there was a small change after one hour, and at 75° a considerable change. The rate of change in concentration at 75° gradually decreased, but was such that at the end of two days the calculated "sorption" value was almost double that at the end of one hour. The probable explanation of the change after one hour is that cooking action liberates acids of such strength that after they combine with the alkali the latter cannot be titrated with hydrochloric acid with methyl orange as indicator. With cooking action taking place at 75° no precise evaluation can be made of the change caused by raising the temperature from 50° to 75°. It may be concluded, however, that the values of the sorption of sodium hydroxide on black spruce are not very much affected by raising the temperature.

The results confirm the work of Richardson and Maass in regard to the first break in their sorption curve for wood. The effect of temperature change on the position of this break in the curve is similar to that observed by Beadle and Stevens (1), and D'Ans and Jäger (4), who worked with pure cellulose.

Along the flat part of the curve, the sorption per gram of cellulose is considerably greater for wood (based on a content of 50% cellulose) than for cotton. The indication is that lignin and other wood substances, in addition to cellulose, take up alkali.

There has been a considerable amount of speculation concerning the interpretation of the curves showing sorption of alkalis on cellulose. Morrison, Campbell, and Maass (6) have found that the heat of sorption of sodium hydroxide on cellulose, when plotted against concentration of alkali, gives a curve having a break at the same concentration as that in the sorption curve.

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THE HEAT CONTENT OF WATER ADSORBED ON CELLULOSE[1]

By J. H. Shipley[2], W. Boyd Campbell[3], and O. Maass[4]

Abstract

The heat capacity of water adsorbed on cellulose has been measured by means of a new type of adiabatic calorimeter and a new experimental technique. Measurements have been made with 2, 4, 8, and 12% adsorbed water over the temperature range −35° to +25° C. with considerable accuracy. A mechanism that of a change in the amount of bound water with the temperature, has been suggested to explain the high values obtained for the apparent specific heats of adsorbed water.

Introduction

From the results reported by the authors in a previous paper (7), and from further results obtained with mercerized cellulose, it seems apparent that there was an error inherent in the original procedure followed in those previous experiments involving measurements made at very low temperatures with cellulose containing adsorbed water. Since the cellulose containing the sorbed water was cooled down very rapidly when the container was plunged into the cold thermostat, it was thought that it would be possible for water to distil from the cellulose to the container wall if there was an appreciable temperature difference between the cellulose and the wall for any length of time. To investigate this possibility, one junction of a thermocouple was embedded in the cellulose and the other was fastened to the container wall, and the leads were connected through a variable resistance to a sensitive galvanometer. On immersion of the sample in the cold thermostat, the temperature differences between the cellulose and the wall were determined at definite time intervals. From tables of percentage relative vapour pressure in a cellulose-water system the allowable temperature difference, under which no distillation would occur, was calculated and found to be 4° C. The rate at which the sample could be cooled down and yet never give a temperature difference greater than 4° C. was found to be 2° C. per min.

Experiments were made to determine the values of the heat capacity of the sorbed water when the sample was initially cooled rapidly and when cooled slowly. There was a considerable difference between the values for a high percentage of adsorbed water, especially at the low temperatures. But it may be pointed out that the results for the heat capacity of dry cellulose and the heat capacity of sorbed water at the higher temperatures are not affected by this factor.

With these disadvantages in mind it was deemed advisable to design a new adiabatic calorimeter that would be suitable for the measurement of the heat capacity of small amounts of sorbed water at low temperatures.

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Contribution from the Department of Physical Chemistry, McGill University, Montreal, Canada. This investigation was carried out in co-operation with the Forest Products Laboratories of Canada, Montreal, and formed part of the research program of that institution.

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Experimental

1. *Description of the Apparatus*

The calorimeter was of the adiabatic-electrical type. Radiation thermels were used to maintain adiabatic control, and it was possible to detect a difference of 0.0001° C. between the temperature of the inner and that of the outer portions of the calorimeter. For the proposed work it was necessary to reduce the losses due to thermal conductance to a minimum, and also to reduce the heat capacity of the calorimeter to a value such that the heat capacity of the sorbed water could be obtained with the desired accuracy. Losses due to thermal conductance were very low, as the only direct connections to the inner container were the three bakelite legs upon which the container stands and the two wires conducting the current to the heating coil.

The novel feature of this calorimeter was that there was no liquid bath around the inner container, the heating coil being wound directly around the copper container. This eliminates the errors due to evaporation of the calorimetric liquid, which is large in the older types of calorimeters. Also, the heat capacity of the apparatus is reduced to a much lower value.

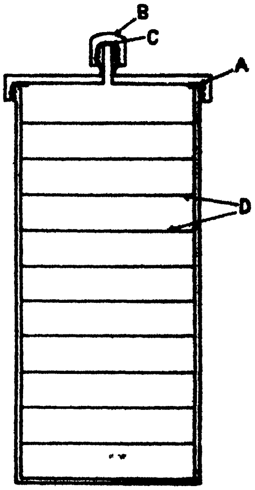

Fig. 1 *Calorimeter vessel*

The container, which is shown in section in Fig. 1, was made in the form of a cylinder of very thin copper, fitted with a cover which screwed on to a rubber gasket, *A*, thus making a vacuum-tight join. There was a small opening in the cover fitted with a screw cap, *B*, and a vacuum-tight join was obtained with a small lead disc *C*. This small opening was used to evacuate and dry the sample after the cover was screwed down, and was later used to introduce water into the sample.

The sample, consisting of a very pure form of bleached sulphite pulp of density 1 57, was cut into discs and packed into the container. Ten copper discs, *D*, of 5 mils thickness were placed uniformly throughout the pulp to aid in establishing thermal equilibrium. The cover was attached and two very thin coats of bakelite varnish diluted with amyl acetate were applied to the container. These were baked on to ensure electrical insulation and still preserve good thermal contact. After the dry weight of the sulphite pulp had been determined by heating to 100° C., evacuating for 14 hr., cooling, and weighing, the resistance element of No. 30 enamelled copper wire was wound non-inductively over the entire container in such a way as to provide uniform heating throughout. The size of wire used was that obtained by calculation to give the required rate of heating. Two coats of bakelite varnish were applied to ensure insulation, and a close-fitting copper cylinder fashioned from 5 mil copper sheet was placed over the coil and container to aid in the attainment of thermal uniformity.

In its final form the container weighed 101.9364 gm., of which 26.6663 gm. was dried sulphite pulp. The calculated heat capacity per degree was 16.6 cal., of which half was contributed by the sulphite pulp. Actually the heat capacity per degree at about 25° C. was found to be about 16.9 cal. The resistance of the heating coil was 10.45 ohms at 23.0° C.

A diagrammatic section of the calorimeter is shown in Fig. 2. The outer jacket, *A*, was made of $\frac{1}{16}$ in. brass and was made vacuum tight by means of six bolts that pressed the lid against a rubber gasket. The central portion was supported on three bakelite legs, *E*, which were cut to a point to minimize thermal conduction. In the space between *A* and *C* was mounted the radiation thermel, *B*, consisting of 13 pairs of junctions, 12 being arranged symmetrically around the sides and one on the bottom. One junction of each pair was supported at a distance of 2 mm. from *C*, and the other was in thermal contact with the jacket, *A*, being electrically insulated from it by a thin piece of mica.

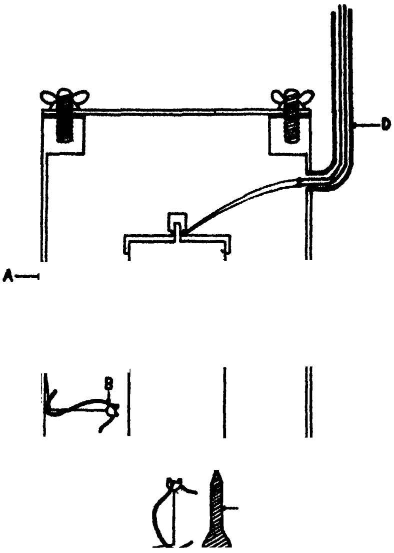

FIG. 2. *Adiabatic calorimeter.*

The size of the wire for making the connections to the resistance coil was of some importance, as the larger the size the greater the thermal conductance for a given temperature difference; on the other hand, if the wire were too fine an appreciable amount of heat would be developed in the connecting wire by the current. A calculation indicated that No. 26 copper wire was the optimum size. These leads were soldered to heavy copper connections that passed out of the apparatus through the brass side tubes, *D*. The leads to the radiation thermel passed through another side tube, the potential leads through a third tube, while a fourth tube was provided for evacuating and for filling the calorimeter jacket with dry air.

The whole assembly was immersed in a well insulated, large vacuum flask containing acetone. Acetone was used because, at low temperatures, water from the air would condense and form ice if it were not soluble in the liquid bath. The acetone was stirred by means of a current of dry air, and the temperature was measured with Beckmann thermometers. The bath was provided with electric heaters for raising the temperature, whereas for lowering the temperature small pieces of solid carbon dioxide were dropped in.

The electrical circuits are shown in a simplified form in Fig. 3. *R* is the calorimeter heater and R_1 a standardized resistance with a very low temperature coefficient of resistance. R_2 is approximately equal in resistance to *R* and is used to draw current prior to a run so as to bring the battery, *B*, to as constant a voltage as possible. R_3 is a variable resistance by means of which the current through the system may be varied; it thus controls the rate at which the temperature rises. The voltage leads to the potentiometer, *P*, are indicated by light lines. The thermels are connected to the sensitive galvanometer, *G*, which has an optical path of about four metres to the scale.

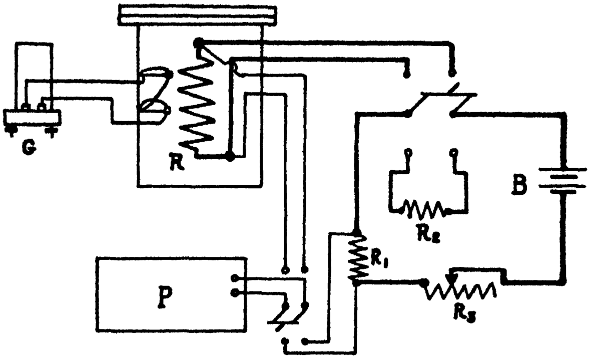

FIG. 3. *Electric connections for adiabatic calorimeter*

By measuring the voltage drops across *R* and R_1 and the time interval during which the current is flowing, the heat input may be calculated from the relation

$$Q = \frac{E_1 \times E_2 \times t}{R_1 \times 4.185} \text{ cal.},$$

where E_1 = potential drop across R_1 (volts),
E_2 = potential drop across *R* (volts),
R_1 = standard resistance (8.627 ohms),
t = time in seconds.

2. *Standardization of Beckmann Thermometers*

Five Beckmann thermometers that were set for use at approximately −35°, −20°, −5°, +5°, and +25° C. were employed in conjunction with this apparatus. The zero point for each was determined by comparison with a calibrated platinum resistance thermometer. In all the experiments the thermometers were used within 0.1° C. of the point at which they had been standardized, and therefore there was no necessity for calibrating them over the entire scale.

3. *Procedure*

The procedure adopted in making a determination of the heat capacity of the container plus contents is as follows. The calorimeter bath was cooled to several degrees lower than the desired initial temperature so that the container and contents could be cooled by radiation and conduction in a reasonable time. The resistance coil around the container proved of immense value as a resistance thermometer in the determination of the approximate temperature of the container. This obviated the necessity of repeatedly bringing about thermal equilibrium by warming the outer bath to determine the temperature of the container. Also, the rate at which the container cooled down could be followed when the sample contained water, and thus any possibility of distillation of water from the cellulose to the cold wall could be guarded against. It was found that owing to the resistance of the air gap between the jacket and the container the maximum rate of cooling of the container was about 1° C. per min., which was well below that causing distillation.

When the container had cooled to the desired temperature the calorimeter was warmed to the required initial temperature by adjusting the temperature of the bath and by passing current through the heating coil. The exact initial temperature was determined by maintaining adiabatic conditions and reading the temperature of the outer bath by means of the suitable Beckmann thermometer The current was then switched on and simultaneously the heaters in the outer bath were started. Adiabatic conditions were maintained by adjusting the current flowing through the bath heaters and also by the use of a spot heater and small pieces of solid carbon dioxide. In this way it was possible to keep the temperature difference between the bath and the inner vessel to about ±0 004° C.

When the temperature had increased to that desired, the current was switched off and the exact time during which it was flowing was recorded. The final temperature was determined in the same manner as the initial temperature. During the course of the determination the voltages across the heating coil and the standard resistance were measured at intervals of 10 or 15 min., and the average values for E_1 and E_2 were employed in the calculations.

It was apparent that heat was conducted into the container along the current and potential leads, thus causing a definite rise in the temperature This was partly overcome by immersing in the outer bath the first two feet of the current leads that projected from the side arm of the jacket.

The temperature rise appeared to the same extent in all the experiments, and therefore did not affect the results, as they were obtained by the difference between two series of runs. The same rate of heating was used at all times, so that the rise in temperature due to this leakage would be the same in all cases.

4. *Introduction of Water to the Sulphite Pulp*

After the total heat capacity of the container plus dry sulphite pulp had been determined, all the electrical connections were broken at the solder joints and the calorimeter was removed from the acetone bath. The container was taken out of the outer jacket, the leads to the coil being separated at the solder joins between the No. 26 connecting wires and the coil proper. The container was then weighed; the difference between this weight and the original was very small, and was due to the solder left on the current leads. The small cap was unscrewed, and redistilled water was introduced in approximately the required proportion by means of a small capillary tube. The cap was replaced and the exact amount of water introduced was determined by weighing.

To ensure an even distribution of the water throughout the pulp, the container was placed in an oven at 50° C. for 10 hr. It was then removed and allowed to stand at room temperature. This was repeated several times, and finally the container was replaced in the calorimeter jacket and the apparatus was reassembled.

5. *Experimental Errors*

For the measurement of time an accurate, calibrated chronometer or a stopwatch calibrated against this chronometer was used. The time interval of an experiment could be measured to 1 part in 20,000. The combined error in e.m.f. measurements was 3 parts in 10,000. The initial and final temperatures could be obtained to within ±0.003° C., and therefore the probable error would be 1 part in 20,000. Over a 60° temperature interval (−35° C. to +25° C.) the probable experimental error is 0.04% in the heat capacity of the container plus contents. This corresponds to an error of about 0.08% in the heat capacity of the dry sulphite pulp.

Therefore the probable error to be expected in the heat capacity of the sorbed water will be 2 5% error for the water sorbed to the extent of 2%, 1 3% error for 4% sorbed water, and 0 7% error for 8% sorbed water.

From the results obtained with dry sulphite pulp over the temperature range −35° to +25° C. it was found that the heat capacity per degree for three successive experiments was 15 719, 15 722, and 15 731 cal. The average value was 15 724 cal. per degree and the mean deviation was ±0.003 cal. This indicated that the error in this average value was 0 02%, which is in very good agreement with the value calculated above, as one would expect the actual error to be less than the calculated probable error.

Results

The total heat capacities of dry bleached sulphite pulp, and of 2, 4, 8, and 12% of adsorbed water were determined over the four ranges of temperature −35° to +25° C., −20° to +25° C., −5° to +25° C., and +5° to +25° C.

In Table I are summarized the mean values of the total heats of the container and contents between the initial temperatures given in Column 1 and the

TABLE I

TOTAL HEATS GIVEN UP BY THE CALORIMETER

(Cal., corrected to a final temperature + 25 00° C)

Initial temp., °C.	Sulphite pulp	Sulphite pulp plus			
		2 0% water	4 0% water	8 0% water	12 0% water
−35 00	944 28	974 67	1002 47	1066 53	1135.01
−20 00	721 74	744 23	766 29	815 38	896 67
− 5 00	489 69	506 33	521 79	555 21	592 75
+ 5.00	330 13†	342 08	353 09	376 30	400.74

† *Calculated value.*

final temperature. Each value reported below is the mean of at least two determinations which agreed to 1 part (or less) in 1000.

The value of the total heat from +5.00° to +25.00° C. for the container plus dry sulphite pulp was determined from the following equation

$$H = 2667.3 + 1.9413T - 0.046548\ T^2 + 0.000033614\ T^2.$$

This equation represents the variation of the total heat content of container plus dry sulphite pulp with the temperature over the range −35° to +25° C. The value obtained by substituting for the temperature in the above equation is good to 1 part in 10,000, as indicated by the agreement between the other points which were determined both experimentally and from the equation.

The heat contents of the sorbed water, per gram of water, are given in Table II. The heat content of "2.0%" water (Column 2, Table II) was obtained by subtracting the values in Column 2 from those in Column 3 of Table I, that is, subtracting the heat content of the container plus dry sulphite pulp from the heat content of the container plus sulphite pulp plus 2.0% of water, and recalculating on the basis of 1 gm. of sorbed water. Similarly the heat contents of the other quantities of adsorbed water per gram of water were determined by subtracting the appropriate values and recalculating on the basis of 1 gm. of sorbed water.

TABLE II

TOTAL HEATS PER GRAM OF SORBED WATER

(Cal., corrected to final temperature + 25.00° C.)

Initial temp., °C.	2% water	4% water	8% water	12% water	4%–2% water	8%–2% water	8%–4% water	12%–8% water
−35.00	57.24	54.72	57.32	59.95	52.21	57.34	59.90	65.30
−20.00	41.40	41.90	43.91	46.50	41.44	44.42	45.90	51.77
− 5.00	30.63	30.19	30.72	32.39	29.05	30.52	31.25	35.80
+ 5.00	22.51	21.59	21.65	22.19	20.67	21.36	21.70	23.31

Discussion of Results

Bleached sulphite pulp was used because it could be obtained in a very compact form, and therefore a large amount could be packed into the container. Also, relative vapour pressure measurements showed that bleached sulphite pulp holds more water by surface adsorption than mercerized or standard cellulose. This would mean that any difference in heat capacity of the first portion of adsorbed water from that of the water subsequently added would be enhanced.

The heat capacities of 2, 4, 8, and 12% adsorbed water on bleached sulphite pulp (Table II) are shown graphically in Fig. 4. The surprising fact that there is no great difference between the heat capacities of the 2, 4, 8, and 12% adsorbed water is readily apparent from Fig. 4. This result was totally unexpected and is absolutely contradictory to previous conclusions made in this laboratory and elsewhere which were based on experiments other than specific heat measurements.

Previous experiments (7) indicated that initially the water adsorbed is very tightly bound and may even be in the form of a surface compound with the cellulose. As water is subsequently added, the bonding becomes less secure and at approximately 8% sorption the water is probably condensing in the capillaries.

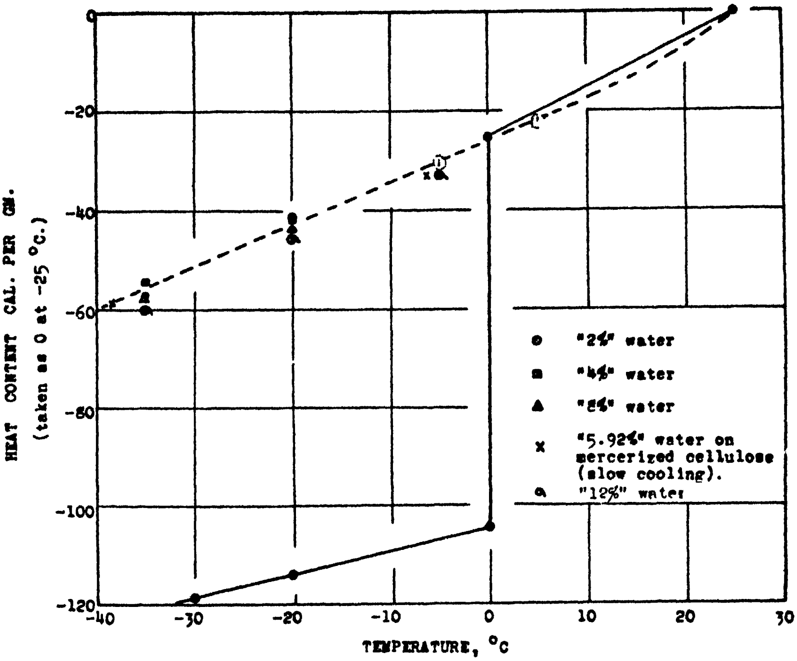

FIG. 4. *Heat content of adsorbed water between +25° C and lower temperatures.*

It may be seen from Fig. 4 that the heat contents of 2, 4, 8, and 12% adsorbed water lie on curves that actually indicate a higher heat content for adsorbed water above zero degrees than the heat content of free water, which is indicated by the solid line. This is most unexpected since previous experiments on dielectric constant (2), heat of adsorption (1), vapour pressure (3, 8), and density (4) indicate that the first portions of adsorbed water are tightly bound. But such water must be partly restricted in movement, and therefore the number of degrees of freedom would be diminished. This would entail a lowering of the heat capacity. But the heat capacity is not lowered. Also, since with increase in water content the proportion of free water must increase, it would be expected that specific heat of the adsorbed water would increase markedly with rise in the quantity of water adsorbed. This also is not the case.

It seems reasonable to suppose that on cooling below 0° C. the adsorbed water will remain adsorbed and will not form ice, so that no latent heats of fusion are to be expected. With increased water content and the existence of free water one would expect a possible heat adsorption due to freezing, although here also it probably would not occur owing to the phenomenon of supercooling when water exists in a state of very fine subdivision (6).

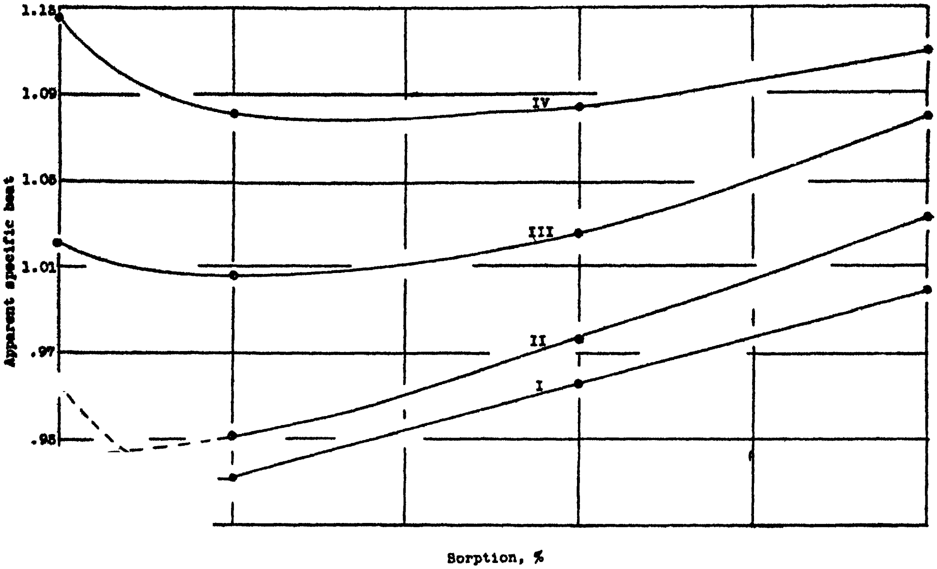

FIG. 5. *Variation of apparent specific heat of adsorbed water with percentage adsorbed. I, −35° to +25° C II, −20° to +25° C. III, −5° to +25° C IV, + 5° to +25° C*

In Fig. 5 the average specific heats of the adsorbed water for the respective temperature ranges are plotted against the percentage of water adsorbed. Curve I is the average specific heat over the range of temperature −35° to +25° C., Curve II for the range −20° to +25° C., Curve III for the range −5° C. to +25° C., Curve IV for the range +5° to +25° C. It will be noticed that the specific heats are plotted on a large scale, so that any experimental error is greatly magnified. Nevertheless all the curves show a marked uniformity except that the values for 2% adsorbed water in Curves I and II seem to be interchanged. It is possible that this is due to experimental error.

The apparent specific heat over the temperature range +5° to +25° C. (Curve IV) is definitely above the specific heat of free water for all values of water content. The same may be said for the range −5° to +25° C., and those at the lower temperatures are not much below the specific heat of free water. The explanation that the high value may be due to the latent heat of fusion has already been ruled out in the previous discussion. Also, it may be seen that the high values for the specific heats are obtained for the range +5° to +25° C., and over this range the temperature has never been brought below the freezing point of water.

As the 2% adsorbed water, most of which must be bound, at least more so than in the higher quantities, gives the highest value for the specific heat at

+5° C., some source of heat absorption must be looked for other than that required for heating up the cellulose and water alone. It is suggested that some change in equilibrium in the system water-cellulose must occur which brings about an absorption of heat when the system is warmed up. Such a mechanism is corroborated by other facts, and it may be of considerable theoretical importance that attention has been drawn to the possibility of this mechanism.

The amount of water that is held by cellulose at any one concentration exists in various degrees of freedom, the term being used in the sense of the extent to which it is bound to the cellulose. It is suggested that a rise in temperature decreases the amount of bound water and increases the freedom of some water to the corresponding extent. The large heat of adsorption that was found by Argue and Maass (1) shows that the change from bound water to free water requires a large amount of heat. In the heat capacity measurements, the heat that was added was therefore required for two purposes, first, the heat capacity of the system as a whole, and second, to supply the heat necessary to bring about a decrease in the amount of bound water with rise in temperature. If this quantity were known and subtracted, the resultant specific heats of the adsorbed water would be less, and probably conform with what could be predicted from the other physicochemical measurements.

Additional evidence that with rise in temperature the extent to which water is bound at a definite concentration decreases is given by the following considerations. It has been found by Urquhart and Williams (9) and by Walker (10) that, except at temperatures above those used in this work, if the relative humidity is kept constant and the temperature is raised, the amount of adsorbed water decreases, or that for a constant amount of adsorbed water the relative humidity has to be increased with rise in temperature in order to keep the water adsorbed. In other words, the vapour pressure of the water adsorbed on cellulose increases relatively, with rise in temperature, more rapidly than the vapour pressure of free water. These experimental results also show that with rise in temperature the adsorbed water becomes less bound.

A somewhat analogous case was found by Horn and Mennie (5) in the system gelatin-water. Heat capacity measurements on gelatin containing much more water than the cellulose in these experiments seemed to indicate that there was a change in the amount of bound water with the temperature.

Conclusions

A new calorimeter and experimental technique have been devised which are applicable to the measurement of the heat capacities of small amounts of water adsorbed on a colloidal material, with a far greater accuracy than was previously possible. The accuracy could be enhanced by a number of alterations in design and by the use of a platinum thermometer with a Mueller bridge for measuring the temperature. In this way it would be possible to increase the temperature range of the measurements.

The heat capacity of water adsorbed on cellulose up to 12% has been measured for the first time over the temperature range −35° to +25° C., with considerable accuracy, but in order to draw any further conclusions from these measurements it is essential to expand previous investigations into the properties of the cellulose-water system. It is suggested that adsorption isothermals be determined on a sample of the cellulose used over a similar temperature range and also that measurements of the heat of wetting over as large a temperature range as is feasible should be carried out.

Since it is possible that there is a change in the cellulose-water equilibrium with rise in temperature, it may be of practical importance that attention has been drawn to this phenomenon, because all paper processing depends to a large extent on the addition and removal of water. Then, if this hypothesis is substantiated, it may prove to be of value in suggesting alterations in conditions, especially in temperature, under which certain parts of the processing are carried out.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XIX. *CORYDALIS OPHIOCARPA* HOOK. f. ET THOMS[1].

BY RICHARD H. F. MANSKE[2]

Abstract

Nine alkaloids have been isolated from *Corydalis ophiocarpa* only one of which, *ophiocarpine*, $C_{20}H_{21}O_5N$ (F39), is definitely characterized as new. It is a hydroxy-canadine in which the hydroxy group probably occurs in position 13. A second alkaloid, which may be new, is referred to as alkaloid F40. Berberine, its tetrahydro-derivative, namely *l*-canadine, and *l*-corypalmine constitute the remaining protoberberine alkaloids that were found. The presence of *l*-adlumine was established. This is the third plant from which it has been isolated. In addition, protopine, α-allocryptopine and cryptocavine, all of which contain the ten-membered ring characteristic of the first, were isolated.

In his latest treatment of *Corydalis*, Fedde (1) has arranged this genus into nine sections, many of which are divided into subsections. It is not the intention of the present author to call into question nor to deprecate such a classification. The fact that it serves as a useful instrument in identification is in itself sufficient justification for its adoption. There are, however, many moot points, and it is unlikely that any system thus far proposed is ultimate.

The possibility that the chemical constituents of plants may aid in their classification has been constantly kept in mind by the author. It is, nevertheless, impracticable to embark upon a program that would include the chemical examination of some 300 species of *Corydalis*. Aside from the labour involved there is the difficulty of securing material. It is feasible, however, to examine representatives of the sections and subsections, and the results obtained may be expected to indicate whether the classification is a natural one.

Thus far the author has investigated some sixteen species of *Corydalis* representing three sections and two subsections. It is expected that papers dealing with a number of these species will be published shortly.

Corydalis ophiocarpa Hook. f. et Thoms. (*C. streptocarpa* Maxim.) is dealt with in this communication. It is placed in the section Eucorydalis Prantl., subsection Strictae Fedde, and is native to Sikkim and to China from Yünnan and Szechwan to Kansu, Shensi, and Hupeh provinces. No American *Corydalis* spp. are placed in the same subsection although most of our species

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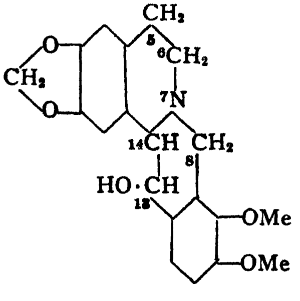
[2] *Chemist, National Research Laboratories, Ottawa.*

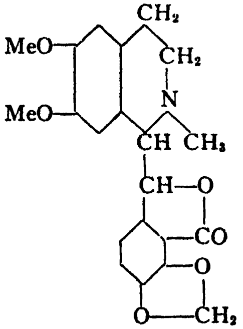
are included in the Eucorydalis section. In this connection it is pertinent to note that *C. aurea* (4) and *C. sempervirens* (3) are placed in the subsection Eucapnoides Fedde of section Eucorydalis. On the basis of their chemical constituents such a close relation is by no means certain. Of a total of some sixteen alkaloids in both species, only two, namely protopine and bicuculline, are present in each of the plants. The protoberberine alkaloids are entirely lacking in *C. sempervirens*. Owing to their widespread occurrence, their complete absence from a particular plant is regarded as significant.

C. ophiocarpa has thus far yielded nine alkaloids, and it resembles *C. aurea* mainly in containing the protoberberine alkaloids. If a reclassification on a chemical basis is attempted at this stage, *C. ophiocarpa* would occupy a position intermediate between *C. aurea* and *C. sempervirens*.

Of the nine alkaloids isolated, only one is definitely new. This is now termed *ophiocarpine* (F39). Analytical figures are in fair agreement with the empirical formula $C_{20}H_{21}O_5N$ containing two methoxyl groups. Two of the oxygen atoms are present in a methylene-dioxy group. A clue to the structure of the alkaloid and to the nature of the fifth oxygen atom was obtained when it was observed that boiling with strong hydrochloric acid resulted in dehydration with the formation of a yellow base which, on oxidation with iodine and subsequent reduction, yielded *dl*-canadine. Ophiocarpine therefore is a hydroxy-canadine in which the hydroxyl group is in one of the three possible positions, namely 8, 13, or 14. Positions 5 and 6 are not considered, because alkaloids in which these positions carry a substituent or are affected by iodine oxidations are unknown. That the hydroxyl is in position 8 is rendered improbable by the facts: (i) that ophiocarpine yields a colourless hydrochloride, and (ii) prolonged heating with alkali induces no appreciable changes. A substance such as 8-hydroxy-canadine bears a close relation to hydrastinine, of which the hydrochloride is yellow and fluorescent and in which a Cannizzaro reaction is easily effected. A hydroxyl group in position 14 seemed *a priori* highly probable. In fact 14-hydroxy-canadine would be tautomeric with N-desmethyl-allocryptopine, a possible alkaloid not yet reported. It is clear, therefore, that the methiodide of 14-hydroxy-canadine would isomerize (tautomerize!) readily to allocryptopine hydroiodide.



(I.)



(II.)

When put to the experimental test, however, ophiocarpine methiodide could not be converted into allocryptopine. There remains therefore position 13 as the most probable for the hydroxyl group in ophiocarpine (I). Such a structure is not entirely without precedent. All the phthalide-isoquinoline alkaloids carry a potential hydroxyl in the benzyl moiety, its position there being strictly analogous to position 13 in the protoberberine alkaloids. Attention has been frequently drawn to the close relation between canadine and hydrastine. It is pertinent to note here that *l*-adlumine (5) has now been isolated from *C. ophiocarpa*. It has the structure (II) in which the positions of the methylene-dioxy and methoxyl groups are reversed with respect to ophiocarpine. Furthermore, *l*-canadine and its oxidation product, berberine, are present, as well as a trace of *l*-corypalmine. It is almost needless to mention that protopine was isolated, but it was accompanied by α-allocryptopine and a very small amount of cryptocavine. This is the fourth plant from which the last has now been isolated (5).

An alkaloid, referred to as F40, was obtained in small amounts. Its adequate identification or characterization is reserved for a later opportunity, as it has been found in larger relative amounts in another species now under investigation.

Experimental

The material for the present investigation was obtained from plants grown in a local garden and at the Central Experimental Farm, Ottawa, and the author takes this opportunity to express his indebtedness to Mr. John Adams of the Division of Botany for providing some facilities for growing the plants. *C. ophiocarpa* is an obligate biennial, and the experiments herein described were carried out with a composite collection comprising the first and second years' growths. There was available a total of 13.7 kilos of dried material. The procedure to which the author has repeatedly referred (2) was employed without modification for the isolation of the alkaloids, and the designations in the following summary have the significance previously adopted.

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,—ophiocarpine (F40), *l*-canadine, alkaloid F39.
BCE and EEC—Phenolic bases precipitated by carbon dioxide,—*l*-corypalmine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—protopine, α-allocryptopine, cryptocavine, *l*-adlumine.
BSE and EES—Phenolic bases precipitated by carbon dioxide,—(not crystallized).

Ophiocarpine and Canadine

The washed and dried fraction (BC) consisted almost entirely of ophiocarpine, and its recrystallization from a large volume of methanol, in spite of its sparing solubility in this solvent, was found to be the best method of purification. A prior washing with cold methanol served to remove a small amount of *l*-canadine, which was obtained pure as the hydrochloride, regenerated from the latter, and recrystallized from methanol (0.01%). Almost colourless fine crystals melting at 135° C.* were obtained. $[\alpha]_D^{22°} = -308$ ($c = 0.28$ in methanol). Calcd. for $C_{20}H_{21}O_4N$: C, 70.80; H, 6.20; N, 4.13; 2OMe, 18.20%. Found: C, 70 80, 70.68; H, 6.41, 6.28; N, 4.45, 4.37; OMe, 18.39, 18.01%.

A specimen was oxidized in ethanol with iodine, and the resulting quaternary iodide reduced with zinc in acetic acid. The *dl*-canadine thus obtained melted at 171° C., either alone or in admixture with a specimen prepared from berberine.

The once recrystallized ophiocarpine (yield, 0.25%) was recrystallized again from methanol, and was thus obtained in large stout prisms melting sharply at 188° C. The hydrochloride is colourless and sparingly soluble in cold water, and the base regenerated from it, and recrystallized as before, melted at the same temperature. It was also recrystallized by evaporating its solution in chloroform to a small volume and adding methanol. The melting point was not changed. $[\alpha]_D^{24°} = -284°$ ($c = 0$ 4 in chloroform). Found: C, 68 00, 67 91; H, 6 04, 6 02; N, 4 30, 4 22; OMe, 15 99, 15 81%. Calcd. for $C_{20}H_{21}O_5N$: C, 67 60; H, 5 92; N, 3 94; OMe, 17.46%. The *methiodide* was slowly formed in a chloroform-methanol solution containing methyl iodide. After recrystallization from boiling water it melted to a black mass at 271° C. It also crystallized from the hot aqueous solution in the presence of ammonia or of potassium hydroxide.

Protopine and α-Allocryptopine

The fraction (BS) was dissolved in chloroform and the filtered solution (charcoal) evaporated to a small volume. The addition of hot methanol and a nucleus induced rapid crystallization of protopine, which was obtained pure by recrystallization (yield 0 19%).

The methanolic mother liquor was boiled with charcoal and evaporated to a small volume. A second crop of protopine crystallized and was filtered off. The addition of a crystal of α-allocryptopine to the filtrate induced the crystallization of this base. It was slightly contaminated with protopine, from which it was separated by recrystallization from much hot methanol. It melted at 160° C., either alone or in admixture with an authentic specimen of α-allocryptopine (yield 0.01%).

l-Adlumine and Cryptocavine

The mother liquor from the separation of the protopine and α-allocryptopine was evaporated and the residue dissolved in dilute hydrochloric acid. The turbid solution was filtered through charcoal, basified with ammonia, and extracted with much ether. The residue from the combined extract was dissolved in a small volume of methanol, from which a copious crop of crystals separated in the course of several days. This was a mixture and consisted of protopine, α-allocryptopine, and *l*-adlumine. The last was separated as follows. A chloroform solution of the mixture was evaporated to a thin resin, which was then dissolved in boiling methanol. A nucleus of pure *l*-adlumine was added. Crystallization of the large elongated hexagons was immediate, and the crystals were filtered off before the other bases crystallized. A second recrystallization from chloroform-methanol yielded *l*-adlumine melting sharply at 180° C., either alone or in admixture with authentic specimens from *C. sempervirens* or *C. scouleri*. The total yield was 0.03%.

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* *All melting points are corrected.*

The mother liquor from the crystallization of *l*-adlumine on long standing deposited a base contaminated with several groups of protopine crystals. The latter were separated by means of a spatula and the main base was recrystallized from chloroform-methanol. A repetition of the process yielded fine colourless needles melting at 223° C. (yield, 0.005%). Admixture with a specimen of cryptocavine from other sources did not lower the melting point, and the optical rotation in chloroform was zero. The colour reaction in sulphuric acid was that of the protopine group.

l-Corypalmine

The fractions (EC, BCE, and EEC) yielded a small amount of a crystalline base when left in contact with methanol. The base was recrystallized from chloroform-methanol and obtained in colourless stout prisms which, either alone or in admixture with a specimen of *l*-corypalmine from *Dicentra oregana*, melted at 230° C., some darkening taking place several degrees lower. The same alkaloid has been obtained in larger amounts from other species under investigation, and its positive identification as *l*-corypalmine will be described in detail in an early communication. The yield in the present case was considerably less than 0 01%.

Berberine

When the residue from the chloroform extract (C) of the aqueous acid solution was extracted with hot water and the filtered solution allowed to cool, a copious yield of a sparingly soluble hydrochloride was obtained. It was recrystallized again from hot water (yield, 0.05%), and a portion of it reduced with zinc dust in acetic acid. The regenerated base was recrystallized from methanol and identified as *dl*-canadine by melting point and mixed melting point (170° C.).

That berberine is contained as such in the living plant is highly probable because of the yellow colour of the sap. In autumn the leaves also take on an orange hue. It seems therefore improbable that oxidation of the *l*-canadine during the process of drying and extracting is the sole source of the berberine.

Alkaloid F40

The mother liquor from the recrystallization of the berberine hydrochloride was concentrated somewhat. On cooling, a mixture separated. This was redissolved in warm water, and an excess of ammonia was added. After cooling, the mixture was filtered and the precipitate washed with warm water until the filtrate was colourless, a procedure that served to remove the berberine. The dried precipitate was recrystallized twice from chloroform-methanol; it then melted at 196° C. This base, *alkaloid F40*, has also been obtained from *C. cheilanthifolia*; its further examination will be detailed in connection with this plant.

Fumaric acid was isolated in small amounts from the ether extract (LC).

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XX. *CORYDALIS MICRANTHA* (ENGELM.) GRAY AND *CORYDALIS CRYSTALLINA* ENGELM.[1]

By Richard H. F. Manske[2]

Abstract

Chemical examination of *C. micrantha* and of *C. crystallina* has shown that their relation is not as close to *C. aurea* as taxonomic classification would suggest. *C. micrantha* was found to contain protopine, *l*-tetrahydro-palmatine, capaurine, capauridine, scoulerine, and three unidentified phenolic alkaloids (F41, F42, and F43). *C. crystallina* yielded only a small amount of total bases from which protopine, bicuculline, and capnoidine were isolated.

The two plants named in the title are evidently closely related taxonomically. Various authors have regarded them as varieties of *Corydalis aurea* Willd.; hence *C. micrantha* (Engelm.) Gray has been referred to as *C. aurea* var. *micrantha* Engelm. or *C. aurea* var. *australis* Chapm., and *C. crystallina* Engelm. is synonymous with *C. aurea* var. *crystallina* Torr. et Gray.

In view of the results of the chemical investigation that forms the subject of this paper, such an extremely close relation is not indicated. *C. micrantha* has yielded eight alkaloids, only four of which, namely protopine, *l*-tetrahydropalmatine, capaurine and capauridine, are also present in *C. aurea* (3). The remaining four alkaloids include scoulerine and three alkaloids, F41, F42, and F43, whose further characterization or identification is dependent upon more material or upon their isolation from other sources.

The small quantity of *C. crystallina* permitted only a preliminary investigation. In addition to protopine there were isolated bicuculline and capnoidine. The last was not found in *C. micrantha* nor in *C. aurea*, and *C. crystallina* has now been found to be the best source of this rare but fairly widely distributed alkaloid. The tetrahydro-protoberberine alkaloids appear to be almost completely absent. It would therefore appear that *C. crystallina* is more closely related to *C. sempervirens* (2).

Experimental

The materials for the present investigation were collected in Texas and kindly placed at the author's disposal by Dr. Glen A. Greathouse, College Station, Texas, to whom grateful thanks are extended. After drying and grinding, the weights were,—*C. micrantha*, 1740 gm. and *C. crystallina*, 1780 gm. The following is a summary of the isolated alkaloids and the fractions from which they were obtained (1), the names in parentheses referring only to alkaloids found in *C. crystallina*.

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[2] *Chemist, National Research Laboratories, Ottawa.*

Base hydrochlorides extracted from aqueous solution by means of chloroform,—

BC—Non-phenolic bases,—*l*-tetrahydro-palmatine (bicuculline).
BCE and EEC—Phenolic bases precipitated by carbon dioxide,—capaurine, capauridine, alkaloid F42, alkaloid F43.

Base hydrochlorides not extracted from aqueous solution by means of chloroform,—

BS—Non-phenolic bases,—protopine (protopine, capnoidine).
BSE and EES—Phenolic bases precipitated by carbon dioxide,—scoulerine, alkaloid F41.

l-Tetrahydro-palmatine

This alkaloid was purified as the sparingly soluble hydrochloride from fraction (BC), and the liberated base was recrystallized from methanol. It was obtained in fine colourless crystals which melted at 142° C.,* and in admixture with a specimen of *l*-tetrahydro-palmatine from *C. aurea* there was no depression in melting point. $[\alpha]_D^{27^\circ} = -281^\circ$ ($c = 2$ in 95% ethanol). The yield was 0 3%.

It has now been observed that *l*-tetrahydro-palmatine, when recrystallized from ether, yields the hydrate which melts with effervescence at 115 to 116° C. This has been found to be identical with an alkaloid previously regarded as new and described as caseanine (5). Mixed melting point determinations of the respective hydrates as well as of the bases recrystallized from methanol showed that they were identical. The optical activity of "caseanine" was found to be identical with that of *l*-tetrahydro-palmatine, and therefore the name, caseanine, no longer has validity. The isolation of bicuculline from fraction (BC) (*C. crystallina*) followed the procedure repeatedly outlined. The yield of pure base was 0 02%. It melted at 177° C. A portion was converted to the higher melting form (196° C.), and both forms were compared with authentic specimens.

Capaurine, Capauridine, Alkaloid F43, and Alkaloid F42

Fraction (BCE) contained coloured impurities which were removed by means of charcoal in methanol solution, and then fraction (EEC) was added. In the course of several days a small amount of fine colourless needles separated. These were recrystallized twice from chloroform-methanol, they then melted at 208° C., either alone or in admixture with a specimen of capauridine from *C. aurea*. The yield of capauridine was 0.006%. The filtrate from the capauridine was evaporated somewhat, and in the course of several days another base (about 0.02 gm.) was deposited. It was recrystallized from chloroform-methanol and obtained in brilliant stout prisms which began to shrink at 226 to 228° C. and melted to a brown tar at 230° C. It does not appear to be identical with *l*-corypalmine, with alkaloid F25, or with alkaloid F32. Unfortunately the analyst lost the sample after having determined nitrogen and methoxyl, so that a carbon-hydrogen analysis could not be carried out

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**All melting points are corrected.*

with the material at hand. The results obtained, however, indicate $C_{20}H_{23}O_4N$. Found: N, 4.30, 4.39; OMe, 26.42, 25.96%. Calcd. for $C_{20}H_{23}O_4N$: N, 4.10; 3OMe, 27.27%.

Alkaloid F43 dissolved in sulphuric acid to yield a colourless solution which, on warming, became yellowish-pink. Progressive heating changed the colour of this solution to orange, then brown, and finally deep purple.

The solvent was removed from the mother liquor from which alkaloid F43 had crystallized, and the residue dissolved in dilute hydrochloric acid. The filtered solution (charcoal) was basified with ammonia, and the liberated bases were extracted with ether. The residue from the ether crystallized readily. It was extracted with several successive portions of hot methanol and the residue recrystallized from chloroform-methanol. Alkaloid F42 as thus obtained consists of fine colourless needles melting at 239° C. with a little previous darkening. Its colourless solution in sulphuric acid only became orange on heating but changed to purple on cooling.

The combined methanolic extract from the purification of alkaloid F42 was evaporated to a small volume. On cooling, pale yellow stout prisms melting at 162 to 163° C. were obtained. When recrystallized again from hot methanol, the base melted at 164° C. Its appearance suggested its identity with capaurine, and a mixed melting point determination (164° C.) proved it.

Protopine and Capnoidine

Except for possible traces of other alkaloids, the fraction (BS) from *C. micrantha* consisted of protopine, which was obtained pure by recrystallization and authenticated by comparison with a genuine specimen. (Yield, 0.06%).

The fraction (BS) from *C. crystallina* was converted into the hydrochloride and most of the protopine isolated as this salt. The regenerated base was properly authenticated, and, together with that obtained from the mother liquor, there was a yield of 0 21%. The filtrate from the protopine hydrochloride was basified with potassium hydroxide and the liberated bases were washed and dried. The mixture was dissolved in chloroform and the filtered solution evaporated to a resin. In contact with methanol the resin crystallized at once. The filtered mixture was redissolved in chloroform, evaporated to a small volume, and treated with hot methanol. The addition of a crystal of protopine induced immediate crystallization of this alkaloid, and when no more appeared to be separating the mixture was filtered. The filtrate deposited almost immediately a second base melting at 235° C. When this was recrystallized from chloroform-methanol, colourless stout prisms melting at 235 to 237° C. were obtained. In admixture with a similarly purified specimen of capnoidine from *C. sempervirens* (m.p. 236 to 238° C.) there was no observable depression in melting point. The yield was 0.025%.

Scoulerine and Alkaloid F41

The fraction (BSE) in methanol was heated with a liberal quantity of charcoal, the filtrate added to fraction (EES), and sufficient methanolic hydrogen bromide added to render the solution acidic. In the course of several days a sparingly soluble salt separated. The free base was regenerated from an aqueous solution of the salt and extracted with ether. The residue from the extract crystallized in contact with methanol-ether. It was washed with a little ether; it then melted at 195 to 196° C. In admixture with a specimen of scoulerine from *C. scouleri* (4) it melted at 198 to 200° C. when placed in a bath preheated to 180° C. (Yield, about 0.01 gm.).

The filtrate from the scoulerine hydrobromide was heated to expel organic solvents, the residue dissolved in hot water, and the turbid solution filtered. A sparingly soluble hydrobromide crystallized from the filtrate in 24 hr. The base was regenerated by means of ammonia and extracted with ether. The residue from the ether crystallized in contact with methanol-ether. It was recrystallized by adding ether to a concentrated methanol solution. Colourless aggregates of fine prisms of alkaloid F41, melting at 177° C. to a red liquid, were thus obtained. It dissolves in cold sulphuric acid to form a colourless solution which, on gentle warming, turns pink. Further heating yields only a brown solution which, however, becomes deep violet on cooling. The yield was about 0.05 gm.

Fumaric acid was isolated from both plants (fraction LC).

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THE ROLE OF COPPER IN THE DETERIORATION OF RUBBER[1]

By R. R. McLaughlin[2] and G. P. Beal[3]

Abstract

Dried rubber latex containing graded amounts of copper ammonium acetate was aged in air (I) and in nitrogen (II), and the deterioration followed by determining the acetone-soluble resin, r, and the relative viscosity of benzene solutions, v. For (I), r decreased slightly for a time, varying inversely with the amount of copper present, increased rapidly to a maximum, and finally decreased somewhat. The value of v decreased rapidly at a rate varying directly with the copper content. For (II), r remained constant, while a slight decrease in v, attributed to traces of oxygen, was of a different order from v for (I). It was concluded that copper, per se, is not deleterious but acts by catalytic oxidation.

As stated in a review of the question by Dufraisse (3, p. 466), oxygen is responsible for at least the more obvious, harmful changes in rubber, as a number of investigators have found slight or negligible deterioration in the absence of oxygen. The deleterious effect of copper on rubber is well known, having first been noted by Miller (4), and it has generally been supposed that this is due to oxidation catalyzed by the copper, an assumption which is in harmony with the above conclusion. In order to test this assumption, this investigation was undertaken. It should be noted that a different conclusion has been reached by Buizov, Molodenskii and Mikhailov (2), who are of the opinion that copper, per se, causes a molecular and micellar disaggregation resulting in stickiness, and that oxygen is not necessary for this process.

The method employed to determine whether the deleterious action of copper is to be ascribed to depolymerization alone or to catalytic oxidation was to carry out parallel experiments involving the addition of cupric ammonium acetate to rubber latex in the absence and in the presence of oxygen, for if it were due to the former cause, there should be evidence of depolymerization in the absence of oxygen. Depolymerizing action was followed by means of relative viscosity measurements of resulting benzene solutions, and oxidation by means of acetone extraction of the resulting resins.

Experimental

Preparation of Samples

Samples were prepared containing 0.10, 0.20, 0.25% copper, by adding cupric ammonium acetate solution (0.00653 gm. Cu per cc.; pH, 10.5) to approximately 75 gm. of 60% rubber latex (pH, 9.6). Samples (10 gm.) of the resulting mixture were placed in Petri dishes 9 cm. in diameter.

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Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Canada.

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The samples to be aged in nitrogen were dried at 35° C. in an atmosphere of nitrogen (freed from oxygen by passage over copper at 300° C.) for three days. The pressure was maintained at about 500 mm. for the first six hours to prevent frothing, and reduced to 50 mm. for the remaining period. The samples were then transferred to a nitrogen-filled, glass container.

The samples to be aged in air were first dried in air at 23° C. for 24 hr., then in the vacuum oven at 32° C. and 50 mm. for two and one-half days. The first samples for measurement were taken after they had been in the drying oven one and one-half days.

Both sets of samples, in Petri dishes, were placed in a room with northern exposure and with rather low light intensity. The samples in air were protected from dust by means of a filter paper suspended two inches above the surface of the dishes; this allowed free access of air.

Acetone Extraction

Acetone was purified by the method of Werner (5) to remove peroxides, and the extraction was carried out for 48 hr. in an Underwriters' extraction apparatus.

Relative Viscosity Measurement

Approximately 0 6 gm samples were weighed out, placed in glass stoppered bottles, and benzene (distilled from sodium) was added in the ratio of 100 gm. of benzene to 1 gm. of rubber. The air was displaced by nitrogen, and the bottles were shaken for 5 to 15 days (as indicated in Table II) till solution was complete. Samples (10 cc) of the resulting solution were placed in an

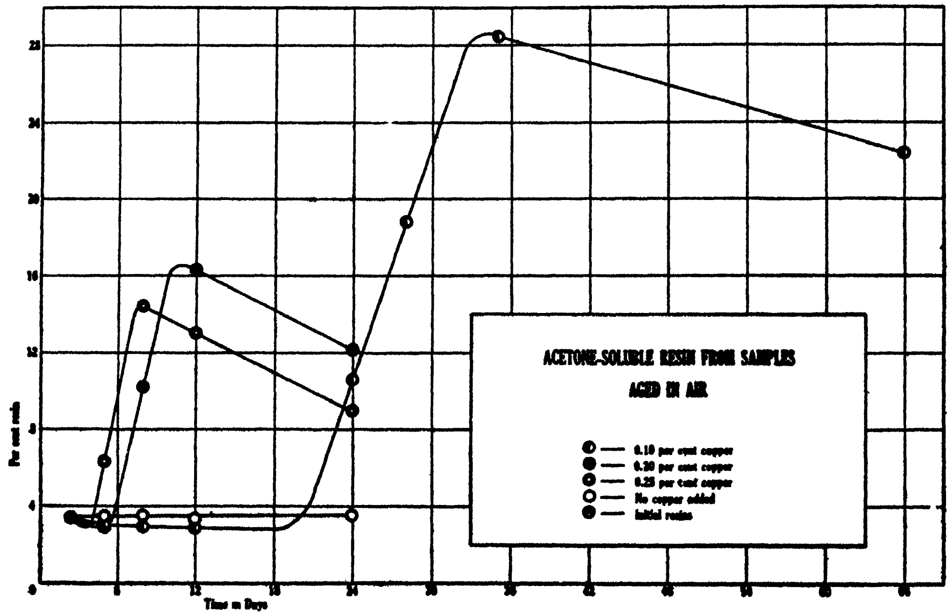

FIG 1. *Graphical presentation of results from Table I, for samples aged in air*

Ostwald viscosimeter immersed in a water thermostat at 25° C., and the relative viscosity was determined by noting the time of flow in seconds. In this time, 3.75 cc. of solution passed through 9 cm. of 1 mm. bore capillary, under a mean head of 10.2 cm.

Discussion

Samples Aged in Air

The curves in Fig. 1 show that there are three distinct stages in acetone-soluble resin production in samples, containing copper, aged in air. *(a)* A period during which the amount of acetone-soluble resin present decreases. This decrease is slight, though it is believed to be significant, and it may be associated with the destruction by the copper of the natural inhibitors of oxidation mentioned by Whitby, Dolid, and Yorston (6) and Bruson, Sebrell, and Vogt (1). The duration of this period varies inversely with the amount of copper present in the samples. *(b)* A period during which resin production begins suddenly and rapidly. During this period the samples become very tacky on the surface, but the rubber next to the glass does not seem to have suffered, a result to be expected from the experiments in nitrogen. *(c)* A period during which the amount of acetone-soluble resin decreases owing to the surface tackiness giving place to a hard skin of material only partially soluble in acetone and benzene.

Correlation of the results given in Tables I and II shows that decrease in relative viscosity runs, in general, parallel with increase in the amount of acetone-soluble resin. The figures indicate that the effect of the copper precedes the actual liberation of acetone-soluble resin, as the relative viscosity begins to fall before the amount of acetone-soluble resin begins to rise. It is likely that this is

TABLE I

ACETONE EXTRACT (RESIN)

Time, days	Copper in samples, %			
	0	0.10	0.20	0.25
	Resin, %			
Aged in air				
2½	3.32 3.36	3.38 3.51	3.36	3.46 3.37
5	3.31 3.55	3.13 3.13	2.85 2.95	5.31 5.96
8	3.33 3.77	2.96 2.96	10.9 9.5	14.25 14.56
12	3.43 3.22	2.78 2.98	18.4 14.3	12.9 13.1
24	3.39 3.69	10.4 10.8	12.0 12.3	7.7 10.3
28		18.5 19.2		
35		28.0 28.9		
66		23.8 21.0		
Aged in nitrogen				
3	3.75 3.88	3.78 3.72	3.72 3.84	3.47 3.73
18	3.27	3.28	3.25	3.26

associated with what might be termed the induction period, *(a)*, mentioned above. It should be noted, however, as will be shown presently, that this step does not appear to take place in the absence of oxygen.

Samples Aged in Nitrogen

As would be expected, the amount of acetone-soluble resin present in the samples aged in nitrogen remained constant throughout.

As the results in Table II show, there is a slight decrease in relative viscosity with time, but this decrease is of a totally different order from that of the samples aged in air. It might be concluded from the decrease, however, that the copper alone has some effect, especially as the relative viscosity at the start varies inversely with the amount of copper present. Another explanation is indicated by the remarks of Dufraisse (3, pp. 463-466) concerning the difficulty of removing all traces of oxygen from rubber samples. It is certain that traces of oxygen either free or in combination, from which it is readily available, would remain in the present case, even though drying was carried out in an atmosphere of purified nitrogen. These traces of oxygen might be quite enough in the presence of copper to account for the diminished viscosity, and it would be expected that the effect would be more pronounced the higher the amount of copper present; and as the residual oxygen is greater since it is unlimited, in those samples dried in air, than in the ones dried in nitrogen, this is a probable explanation for the greater relative viscosity, at the start, of the copper-free samples aged in nitrogen compared with the copper-free samples aged in air. The reason for the relative viscosity of the samples containing copper and aged in nitrogen being progressively lower than that of the copper-free samples, as the amount of copper is increased, is undoubtedly related to this, as the curves in Fig. 1 show that the action of oxygen becomes evident sooner as the amount of copper is increased. In general it is believed that in experiments of this kind a good deal of the deterioration takes place within

TABLE II

Relative viscosity measurements*

Time, days	Copper in samples, %			
	0	0.10	0.20	0.25
	Time of flow, in seconds			
Aged in air				
2½	72.0	42.8	13.8	12 0
7	73.4	29.6	5.6	5.2
12	70.2	13.2	6.0†	6.2†
26	66.4	4.2	7.4†	7.2†
Aged in nitrogen				
7	108	72.2	65.4	51 2
26	108	79.4	53.0	51 8
42	102	60.2	47.2	44 8
164		64.2	54.2	43.2

Time of flow for benzene, 3.7 sec.

**Times allowed for samples to dissolve in benzene:*

Aged in air, without copper, 12 days; aged in air with copper, 4 days.

Aged in nitrogen without copper, 15 days; aged in nitrogen with copper, 10½ days.

†*Insoluble resin present.*

a short time after mixing because of the presence of oxygen during the initial evacuation and drying.

A qualitative observation in support of the conclusions reached is that the samples containing copper and aged in nitrogen had, even after 150 days, retained their initial elasticity and had not become tacky. Furthermore, the samples aged in nitrogen retained their original pale green colour, whereas the samples aged in air turned brown, like those of Buizov, Molodenskii, and Mikhailov (2).

It will be noticed that the times taken for the samples to go into solution provide a rough measure of the relative viscosity to be expected, and support the belief that, in the absence of oxygen, copper has no deleterious action.

Thus, the evidence presented indicates that the deleterious action of copper is not due to depolymerizing action merely because of its presence, but is due to oxidation catalyzed by the copper.

Acknowledgments

This research was proposed and the preliminary work carried out by W. R. Grant as his thesis for the degree of B.A.Sc., obtained in this Department in the academic year 1935–36. The preliminary work was continued by A. B. Lewis for his B.A.Sc. degree in 1936–37.

The completion of the work was made possible by a grant from the School of Engineering Research, University of Toronto.

The rubber latex used was supplied by the Dunlop Tire and Rubber Goods Company, Limited, Toronto.

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SOME OBSERVATIONS ON THE DETERMINATION OF IRON AND COPPER IN BIOLOGICAL MATERIAL BY PHOTOELECTRIC COLORIMETRY[1]

By W. E. Parker[2] and F. P. Griffin[3]

Abstract

The dipyridyl method of estimating available iron has been modified so that it can be applied directly to coloured extracts of plant tissues. By combining the dipyridyl method for iron with the carbamate method for copper, interference of iron with the copper determination has been eliminated and the simultaneous estimation of iron and copper on the same sample made possible.

Introduction

In a study being made in this laboratory of the distribution of iron in plant tissue, it was observed that Elvehjem's (4, 10) method for available iron gave erratic results when applied to acid extracts of leaf tissues. Investigation showed that the discrepancies were due to the introduction of lead acetate as a clarifying agent. It was found that this difficulty could be readily overcome by the use of the Evelyn photoelectric colorimeter (6), and a suitable filter, since then there is no need to clarify the solutions whose colour intensities are to be measured.

The total copper content of the tissues was determined by the carbamate method. McFarlane (9) suggests that isoamyl alcohol be used as the solvent for the yellow copper carbamate complex. However, iron, if present, interferes by the formation of a yellow-brown carbamate salt, likewise soluble in isoamyl alcohol. This difficulty can be overcome by the preliminary conversion of the iron into an un-ionized ferric complex which does not react with the carbamate reagent (3, 7, 9).

Ferrous dipyridyl is un-ionized, and is completely insoluble in isoamyl alcohol. Conversion of the iron into this form should therefore be a suitable method of eliminating its interference with the carbamate reaction. As values for both total iron and copper were desired, it occurred to the authors that the use of dipyridyl, according to Hill's method (8), might permit the simultaneous determination of iron and copper in the one solution. Preliminary experiments showed that the addition of dipyridyl and a reducing agent to a solution containing both iron and copper, followed by the addition of carbamate and extraction with isoamyl alcohol, gave a clear pink aqueous layer and a clear golden-yellow alcohol layer. Measurements of the intensity of the two colours showed that both iron and copper could be recovered quantitatively, even when one was present in large excess.

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The two procedures are described below; that for the combined copper and iron determinations is given in some detail, as there is no reference in the literature to the application of the photoelectric colorimeter to the determination of copper by the carbamate procedure. The golden-yellow colour of the copper carbamate salt is very difficult to measure in an ordinary colorimeter, and it is found that the photoelectric type of instrument increases the accuracy and extends the range of the method.

Modified Procedure for Determining "Available Iron"

Duplicate samples of about 0.2 gm. of the dried and finely ground tissue were weighed into 6 by 1 in. Pyrex test tubes, 10 ml. of 10% acetic acid and 0.1 gram of sodium hydrosulphite* were added, and the tubes heated in a boiling water bath for 15 min. The acetic acid extracts were decanted through Jena glass filters into 50 ml. volumetric flasks and the residues extracted twice more for five-minute periods with the same quantity of acetic acid, and finally with 5 ml. of distilled water. Tests showed that further extraction did not increase the amount of soluble iron. The combined extracts were made up to volume with normal ammonium acetate solution of pH 6.4.

After tubes containing pipetted aliquots of these solutions had been placed in the photoelectric colorimeter fitted with an Evelyn 520 filter, the instrument was adjusted to give a maximum scale deflection of the galvanometer. Exactly 0.5 ml. of a 0.2% solution of α-α'-dipyridyl in 10% acetic acid was then added, the contents of the tube were well mixed, and the reading of the galvanometer again noted. Any decrease in the galvanometer reading was attributed to the presence of ferrous dipyridyl. The iron content of the aliquot was obtained from a calibration curve (5), allowance being made for the dilution by the 0.5 ml. of dipyridyl reagent. The slight error caused by the dilution of the leaf pigments by the reagent was found to be negligible.

Simultaneous Determination of Total Iron and Copper

The strongly acid solution obtained by the wet digestion of the sample (1) was diluted with distilled water and boiled for two minutes to ensure that all the iron was in a form that would react with dipyridyl (2). It was then filtered into a 50 ml. volumetric flask through an ash-free filter paper to remove any siliceous matter which might have been present. To the clear solution were added 0.5 ml. of *p*-hydroxyphenylglycine solution, 1 ml. of α-α'-dipyridyl reagent and then concentrated ammonium hydroxide until the red colour of the ferrous dipyridyl developed. Normal ammonium acetate solution was added to make the mixture almost up to volume, followed by two drops of a 1.5% aqueous solution of sodium diethyldithiocarbamate, and the whole was finally made up to volume with the acetate solution and well mixed. This order of adding the reagents was found to give the most satisfactory results.

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* *In later work 0.5 ml. of a 0.1% solution of p-hydroxy-phenylglycine in 0.4 N sulphuric acid was used as a reducing agent. Campbell and Dauphinee's (1) observations of its advantages have been fully confirmed.*

To a 10 ml. aliquot of this solution in a dry Evelyn colorimeter tube were added exactly 5 ml. of pure isoamyl alcohol. The tube was stoppered with a paraffin-coated cork and the contents mixed by gentle shaking for one-half minute. A clear separation between the two layers took place on standing at room temperature for 15 to 30 min.; centrifuging at 1500 r.p.m. for 15 to 30 sec. gave the same result and avoided the possibility of errors arising from evaporation of the alcohol. It was found that there was no danger of breakage if the colorimeter tubes were fitted by means of cork stoppers into 100 ml. centrifuge tubes.

At this point the two layers can be separated completely and the coloured solutions compared with standards in an ordinary colorimeter. However, when an Evelyn photoelectric colorimeter is available it is much more accurate and convenient to make the measurements without carrying out the separation. In this way all possibility of mechanical loss is avoided, and the advantages of the photoelectric colorimeter for measuring the yellow colour are obtained.

To permit measurements of the two phases in one colorimeter tube, the Bakelite sleeve in which the tubes are inserted was replaced by one having two sets of apertures at right angles to each other and accurately located so that the lower aperture was opposite the aqueous phase and the upper aperture opposite the alcohol phase when the colorimeter tube was inserted in it. The dimensions of the tube, which was constructed of Bakelite tubing, are shown in Fig. 1.

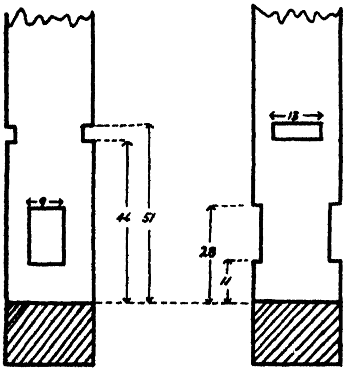

FIG. 1 *Sketch of modified sleeve used in the Evelyn Photoelectric Colorimeter for simultaneous iron and copper determinations. All dimensions are given in millimetres*

The special sleeve was placed in the colorimeter so that the lower aperture was opposite the light source, an Evelyn 520 filter was inserted, and the concentration of iron determined in the usual manner (5). The Evelyn 520 filter was then replaced by an Evelyn 420 M filter, and the sleeve rotated a quarter turn and lowered so that the upper aperture was opposite the light source. A tube containing 15 ml. of isoamyl alcohol was inserted, and the galvanometer deflection adjusted to give a reading of 100 0. The control tube was then replaced by the sample, and the reading of the galvanometer noted. The concentration of copper in the alcohol phase was determined from a previously prepared calibration curve (Fig. 2).

A study of this procedure confirmed McFarlane's (9) findings that the copper carbamate salt is quantitatively extracted by the isoamyl alcohol, and that the colour intensity then follows Beer's law. The latter point is well illustrated in Fig. 2, in which the concentration of copper, plotted against $2-\log G$, is shown to be a straight line over the range 0–4.5γ of copper per ml. Experiments on the recovery of copper and iron from mixtures of the two have shown that 3.35γ of added copper can be quantitatively recovered from a mixture containing 104γ of iron, and that 7.35γ of iron added to a solution containing 47.25 γ of copper can be quantitatively recovered. The method can be applied to solutions containing from 0.2–2.0γ of iron and from 0.2–2.25γ of copper per ml. For concentrations of iron greater than 2γ per ml., the aqueous layer was diluted with a suitable volume of water before the iron determination was made and after the copper reading had been taken.

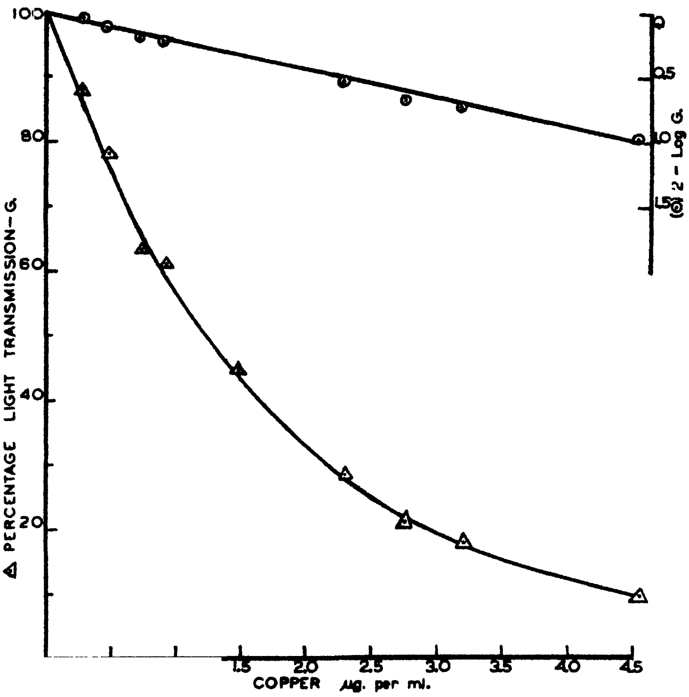

FIG. 2. *Calibration curve and application of Beer's law.*

The second procedure has also been used to determine the amount of free copper in Bordeaux sprays. It was found that the high concentration of calcium in the solution caused the golden-yellow colour of the copper carbamate to fade rapidly. This difficulty could be overcome by using a large excess of the carbamate reagent; the addition of 0.1 gm. of solid sodium diethyldithio carbamate to the final test solution gave a stable colour and reproducible results. It is possible that this difficulty may be experienced in the determination of copper in materials that contain a large amount of calcium.

Acknowledgments

The authors are indebted to Prof. W. D. McFarlane for his advice and criticism, and to Dr. J. A. Dauphinee, University of Toronto, for many helpful suggestions.

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THE SYSTEMS CHRYSENE-1 : 2-BENZANTHRACENE AND 1 : 2-BENZANTHRACENE-TRIPHENYLENE[1]

BY M. G. STURROCK[2] AND T. LAWE[3]

Abstract

The liquidus-solidus curves of the systems chrysene-1 : 2-benzanthracene and 1 : 2-benzanthracene-triphenylene are given. They provide a convenient method for the evaluation of the percentage composition of these mixtures.

In the course of an investigation on the composition of high boiling coal tar oils by fractional distillation, one large fraction was found to be a prolific source of some lesser known coal tar hydrocarbons. In addition to chrysene, its isomers 1 : 2-benzanthracene and triphenylene were obtained in good yield. The liquidus-solidus curves provide a convenient method for the evaluation of the percentage composition of chrysene-1 : 2-benzanthracene and 1 : 2-benzanthracene-triphenylene mixtures. Chrysene-1 : 2-benzanthracene mixtures form a continuous series of solid solutions in which all freezing points lie between the freezing points of the pure components. 1 : 2-Benzanthracene-triphenylene mixtures form a discontinuous series of solid solutions in which the freezing point curve exhibits a eutectic point at 130° C. at 63% 1 : 2-benzanthracene.

The short range fraction boiling at 310° C. at 40 mm. pressure (440° C. at 760 mm.), obtained by fractionation of the crude heavy oil at 10 mm. pressure through an efficient column filled with Stedman wire gauze packing (10), was crystallized from benzol. The first product was chrysene. Subsequent crops of crystals obtained by evaporation of the chrysene mother liquor proved to be crude 1 : 2-benzanthracene. When no further crystals were obtainable, alcohol was substituted for benzol as the solvent. A mixture of 1 : 2-benzanthracene and triphenylene separated from the alcohol, from which pure triphenylene was easily prepared by further crystallization from the same solvent.

The chrysene was purified by crystallization from benzol after removal of the chrysogen by absorption from benzol on a tower of activated alumina; pale yellow lustrous plates showing blue fluorescence in daylight, m.p. 255°C. corr.; quinone, 239° C. corr.; complex with trinitrobenzene, 192 to 194° C. corr. The melting points given in the literature for chrysene and these derivatives are as follows:—melting point, 248 to 249° C. (4), 251 to 252° C. (6), 256° C. (11); the quinone, 239° C. (6); complex with trinitrobenzene, 194 to 195° C. (9). The 1 : 2-benzanthracene was brought to about 98% purity

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by fractional crystallization from alcohol, at which point it was found convenient to complete the separation from chrysene by the formation of a maleic anhydride-1 : 2-benzanthracene adduct (3). The pure hydrocarbon was recovered from the adduct as colourless plates showing a faint blue fluorescence in daylight; m.p., 160° C. corr.; picrate, 142° C. corr.; styphnate, 152° C. corr.; quinone, 166° C. corr. The following values are given for 1 : 2-benzanthracene and these derivatives—m.p. 158.5 to 159.5° C. (4), 155 to 157° C. (6), 159° C. (2), 160.5° C. (5); picrate, 142 to 143° C. (6), 141.5 to

TABLE I

MELTING POINTS AND FREEZING POINTS OF THE SYSTEM CHRYSENE-1 : 2-BENZANTHRACENE

Chrysene, %	1 : 2 Benzanthracene, %	M.P., °C., corr.	F.P., °C., corr.
0	100	160	160
10	90	163	175
25	75	169	197
40	60	178	214
50	50	188	223
60	40	195	232
75	25	211	243
90	10	232	252
100	0	255	255

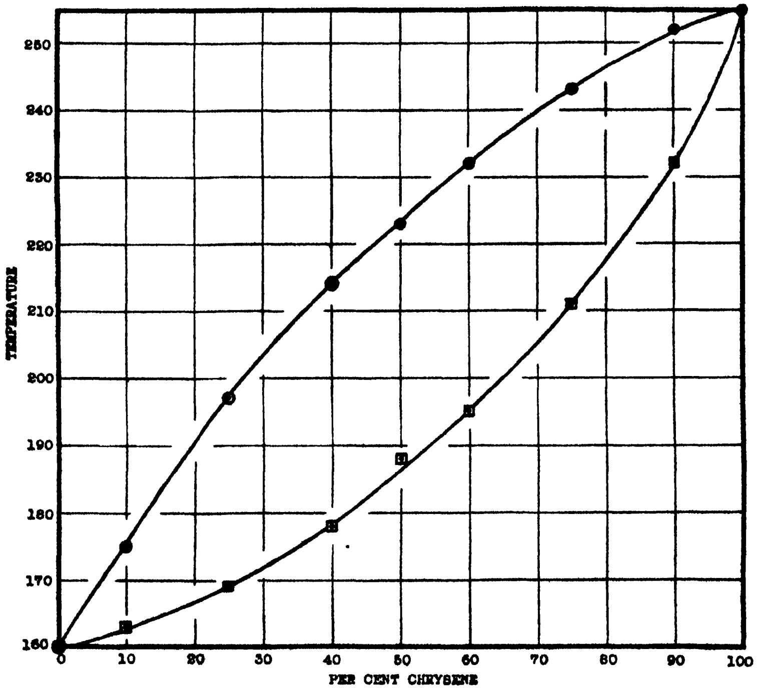

FIG. 1. *Chrysene-1 : 2-benzanthracene liquidus-solidus curves.*

142.5° C. (2); styphnate, 153° C. (2); quinone, 165 to 167° C. (6), 168° C. (2). The triphenylene, long colourless needles from alcohol, melted at 197° C. corr. The melting points given for triphenylene are 196° C. (8), 196.5° C. (7) and 198° C. (1).

The determinations were carried out on known mixtures of the pure components which were melted together, mixed, allowed to solidify and finely pulverized. The melting points and freezing points were obtained by determining the temperatures of incipient fusion and complete liquefaction by the capillary tube method, the temperature being raised very slowly and the material observed through a low power microscope.

TABLE II

MELTING POINTS AND FREEZING POINTS OF THE SYSTEM 1 : 2-BENZANTHRACENE-TRIPHENYLENE

1 : 2 Benzanthracene, %	Triphenylene, %	M.P., °C., corr.	F.P., °C., corr.
0.0	100.0	197	197
25.0	75.0	152	184
27.5	72.5	139	183
30.0	70.0	130	181
50.0	50.0	130	154
63.0	37.0	130	131
65.0	35.0	130	132
75.0	25.0	130	141
80.0	20.0	130	146
85.0	15.0	131	150
90.0	10.0	148	154
100.0	0.0	160	160

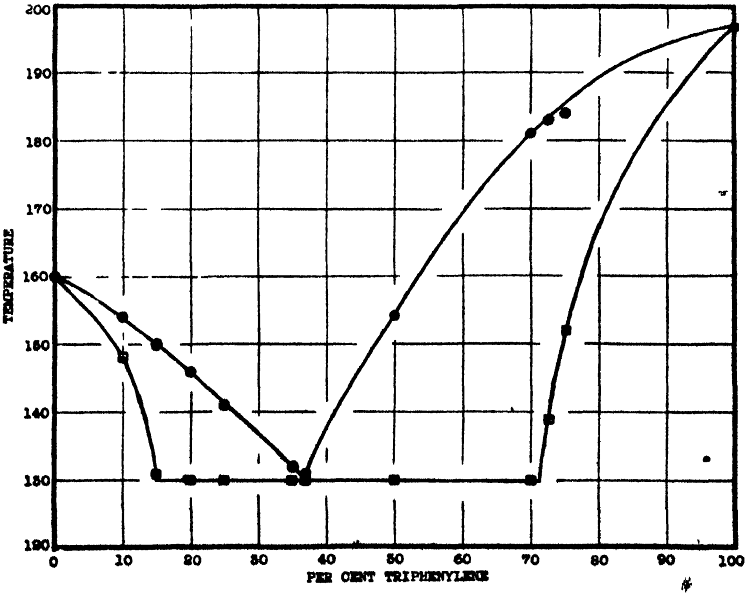

FIG. 2. *1 : 2-Benzanthracene-triphenylene liquidus-solidus curves.*

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2,3-DIPHENYLBUTADIENE-1,3[1]

BY C. F. H. ALLEN[2], C. G. ELIOT[3] AND A. BELL[4]

Abstract

2,3-Diphenylbutadiene has been prepared and its behaviour in addition reactions investigated. It forms a 1,4-dibromide, a 1,4-monobromide by addition of one molecule of hydrogen bromide, is reducible to the saturated hydrocarbon, combines with oxides of nitrogen to form two isomeric dinitrobutenes, and couples with diazonium compounds. In the diene synthesis, products have been secured from maleic anhydride, acetylene dicarboxylic ester, quinone, and α-naphthoquinone. In so far as comparable reactions have been examined, 2,3-diphenylbutadiene resembles 2,3-dimethylbutadiene in the types of products formed by addition. Certain discrepancies recorded in the literature among related dibromides have been cleared up.

While investigating the action of acidic reagents on pinacols, Thörner and Zincke (21) heated acetophenone-pinacol (I) in a sealed tube with acetic anhydride and obtained a hydrocarbon, $C_{16}H_{14}$, which proved to be 2,3-diphenylbutadiene (II). Owing to the low yield and its ease of polymerization, it was not further studied. This work was repeated by Johlin (10) who found that the procedure gave erratic results, a ketone (III), formed by a pinacolone type of rearrangement of the diol, frequently being obtained; the melting points of the ketone and the diene were fairly close and the identity of the reaction products was not easily determined. Johlin reported, incorrectly, that the diene would not add bromine.

Stobbe (20, p. 300) treated the pinacol (I) with acetyl bromide, followed by phosphorus pentabromide and, with difficulty, obtained a dibromide, $C_{16}H_{14}Br_2$, which he thought was (IV) but which is shown below to be (VI). Obviously the reaction proceeds through the intermediate formation of the diene, which it has been found possible to obtain in a yield of 30% by working up the mixture produced by the acetyl bromide treatment. On account of its tendency to polymerize, the hydrocarbon is best kept in the form of its dibromide.

Beschke (3, pp. 120, 149) thought he had obtained this diphenylbutadiene, as a result of removing bromine from the dibromide (IV) with zinc; but, as will be shown below, his hydrocarbon was the *cis*-dimethylstilbene (V). Lévy (12, pp. 878, 890) prepared *trans*-2,3-diphenylbutene-2 (V) and a dibromide from it. Ott (15, p. 2135) secured what he considered to be the

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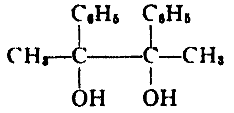
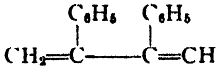
cis-form of this hydrocarbon (V) and the isomeric 1-butene by controlled catalytic reduction of 2,3-diphenylbutadiene.



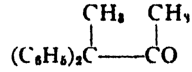
$\mathrm{CH_3{-}\underset{OH}{\overset{C_6H_5}{C}}{-}\underset{OH}{\overset{C_6H_5}{C}}{-}CH_3}$

(I)



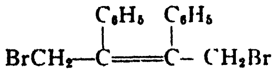
$\mathrm{CH_2{=}\overset{C_6H_5}{C}{-}\overset{C_6H_5}{C}{=}CH_2}$

(II)



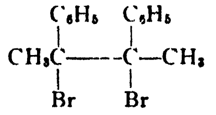
$\mathrm{(C_6H_5)_2\overset{CH_3}{C}{-}\overset{CH_3}{C}O}$

(III)



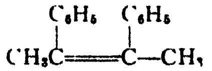
$\mathrm{BrCH_2{-}\overset{C_6H_5}{C}{=}\overset{C_6H_5}{C}{-}CH_2Br}$

(VI)



$\mathrm{CH_3\underset{Br}{\overset{C_6H_5}{C}}{-}\underset{Br}{\overset{C_6H_5}{C}}{-}CH_3}$

(IV)

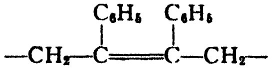


$\mathrm{CH_3\overset{C_6H_5}{C}{=}\overset{C_6H_5}{C}{-}CH_3}$

(V)

In this paper the preparation and reactions of 2,3-diphenylbutadiene are described, and the apparent confusion and uncertainties among the dibromides and related substances are cleared up. Preliminary studies showed that Johlin's procedure was unsatisfactory on account of the low yield and erratic behaviour. On the assumption that the amount of polymer might be decreased by the use of antioxidants, several of these were added to the contents of the sealed tube before heating; phenyl-β-naphthylamine proved to be the most useful. Instead of appreciably reducing polymerization, however, this prevented the rearrangement to the ketone, thus making it possible to secure the diene in each run. Even so, this procedure is less convenient than the reaction between the pinacol and acetyl bromide.

The polymer, on destructive distillation, gave acetophenone, dimethylstilbene, and a tar. This suggests that the structural unit is



$\mathrm{{-}CH_2{-}\overset{C_6H_5}{C}{=}\overset{C_6H_5}{C}{-}CH_2{-}}$

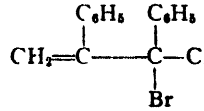
Since the pure stilbene can be distilled without decomposition, the acetophenone may have come from one of the terminal groups of the polymer.

2,3-Diphenylbutadiene readily added one molecule of bromine in a variety of solvents to form a single dibromide. Upon ozonolysis of the dibromide, phenacyl bromide was formed; there was no evidence for any formaldehyde, which was especially looked for. This indicates that the dibromide is correctly represented by the structure (VI), and probably results from the 1,4-addition of bromine. As confirmatory evidence, may be mentioned the fact that it can be recrystallized without change from alcohol. An exact repetition of Stobbe's procedure gave this same dibromide. We suspect that Johlin's failure to secure a dibromide by addition may be attributed to the fact that he unknowingly had the ketone; the melting points of the diene and pinacolone are close, and the two substances are easily confused.

The isomeric dibromides (IV) were obtained by the addition of bromine to the *cis*- and *trans*-dimethylstilbenes (V). One form had been described previously by Lévy (12, pp. 878, 890); the other is new. Both isomers furnished the *cis*-stilbene on removal of the bromine by zinc. This latter reaction thus serves to differentiate the dibromides (IV) and (VI), since the unsharp melting points, which lie in the same range, are accompanied by decomposition; even so, mixed melting points are depressed. The identification of the dibromides, therefore, involves the determination of melting points, removal of bromine by zinc, and determination of the melting points of the hydrocarbons, alone and on admixture. In this way it was shown that Beschke had correctly represented his dibromide as one form of (IV), but that the hydrocarbon, resulting from the action of zinc, was *cis*-dimethylstilbene, and not the diene (II) as he thought.

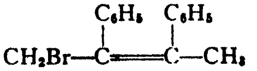
Ott has already described the products resulting from catalytic reduction of 2,3-diphenylbutadiene without details (15, p. 2135); these were to be included in a subsequent paper (that has not yet appeared). He stated that complete reduction gave a mixture of the saturated 2,3-diphenylbutanes, whereas with one equivalent of hydrogen, a mixture resulted, as mentioned above. The former result has been confirmed, but with the latter reaction considerable unchanged diene was recovered, while the residual oil had the characteristic odour of *d,l*-2,3-diphenylbutane. The diene was unaffected by 3% sodium amalgam; sodium in liquid ammonia gave the *meso*-butane and a trace of an unidentified hydrocarbon that did not decolourize bromine. The butanes were synthesized, for purposes of comparison, by a Wurtz reaction from α-bromoethylbenzene.

When a chloroform solution of 2,3-diphenylbutadiene was saturated with hydrogen bromide, a monobromide was obtained; this was also secured from the mixture furnished by the action of acetyl bromide on the pinacol (I). Hydrogen bromide was very easily removed by alcoholic or aqueous solutions, and it gave an immediate precipitate with silver nitrate. These reactions, and its preparation from the pinacol by means of acetyl bromide, would suggest Structure (VII), which could have been formed by a 1,2-addition of hydrogen bromide to the diene. However, ozonolysis of the substance furnished acetophenone and phenacyl bromide, but no detectable formaldehyde; hence it must be a 1,4-addition product as shown in (VIII). Confirmation of this structure was given by the production of the known (4) 3-methyl-2-phenylindene (IX) when the bromide reacted with zinc.



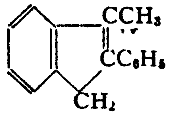
$CH_2{=}C(C_6H_5)-CBr(C_6H_5)-CH_3$

(VII)



$CH_2Br-C(C_6H_5){=}C(C_6H_5)-CH_3$

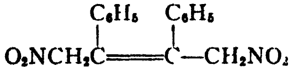
(VIII)



(IX)

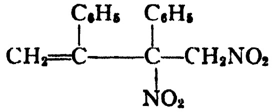
There is no evidence to indicate whether the bromide (VIII) is formed directly by addition at the ends of the conjugated system or by a rearrangement of an intermediate 1,2-addition product (VII). The mode of addition of hydrogen bromide to the diene did not seem to be appreciably affected by the presence of catalysts. The yield was the same when ascaridole or phenyl-β-naphthylamine was present, and but slightly less with thiophenol.

Wieland and Stenzl (25, 26) showed that 1,4-diphenylbutadiene added oxides of nitrogen in the 1 and 4 positions to give a dinitro derivative. This has been repeated and confirmed. 2,3-Diphenylbutadiene also added oxides of nitrogen and gave a pair of substances analyzing for the addition of 2 NO_2. The lower melting isomer formed a disodium derivative immediately, and hence must be one of the two possible 1,4-addition products (X). Upon permanganate oxidation, the higher melting form yielded benzil, while ozonolysis furnished formaldehyde; hence, it must have the structure (XI). It was slowly converted by sodium methylate into a disodium derivative that on acidification yielded the 1,4-addition product (X); this is equivalent to a rearrangement of the allylic type, and probably the first instance in which such a shift of a nitro group has been observed. Neither isomer was affected by hydrogen bromide. It appears, then, that both 1,2- and 1,4-additions have taken place with this diene and oxides of nitrogen.



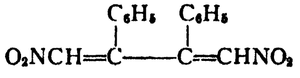
$O_2NCH_2\overset{C_6H_5}{C}=\overset{C_6H_5}{C}-CH_2NO_2$

(X)



$CH_2=\overset{C_6H_5}{C}-\underset{NO_2}{\overset{C_6H_5}{C}}-CH_2NO_2$

(XI)



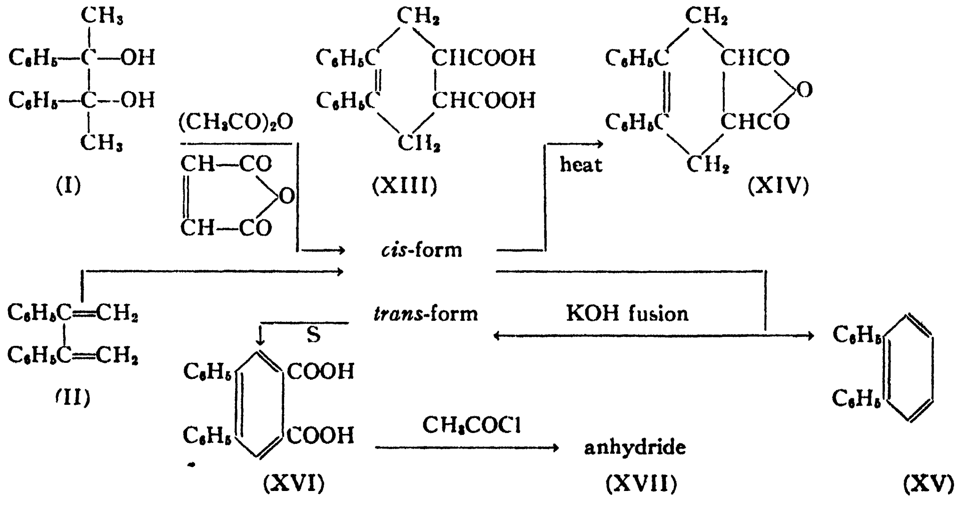
$O_2NCH=\overset{C_6H_5}{C}-\overset{C_6H_5}{C}=CHNO_2$

(XII)

When the sodium salt of the dinitro derivative was treated with bromine, a yellow substance was formed. Analysis showed that this substance differed from the starting material by two hydrogens. Since it was easily oxidized to form benzil, it is the dinitrodiene (XII).

2,3-Diphenylbutadiene coupled with diazotized 2,4-dinitroaniline and picramide, but the coloured products were unstable and could not be prepared analytically pure

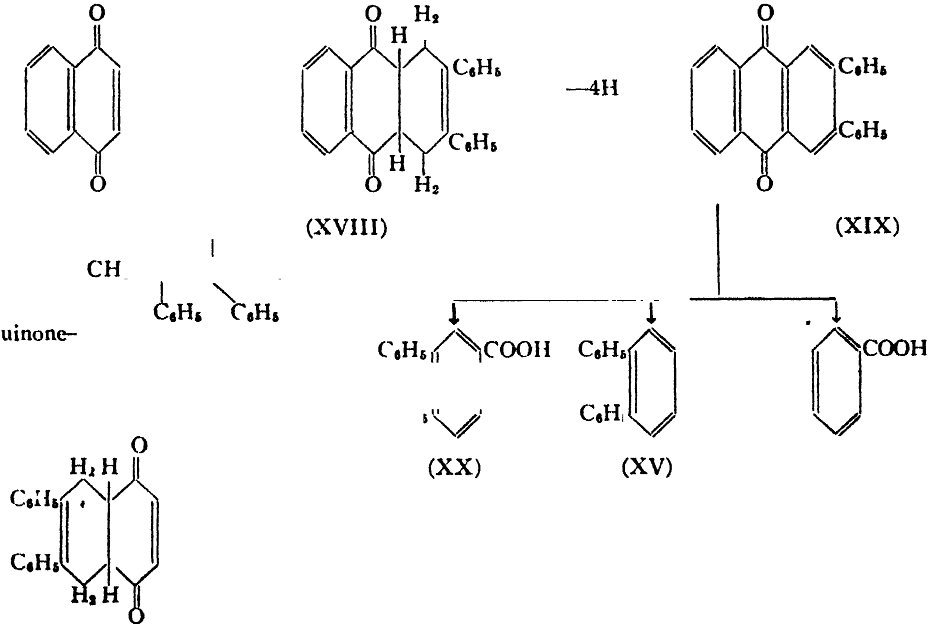
When examined with addends commonly employed in the diene synthesis, the diene was largely recovered unchanged; there seemed to be little tendency towards the formation of an addition product in most instances. The only useful second components proved to be maleic anhydride, quinone, and α-naphthoquinone. The series of reactions involving maleic anhydride and related substances is conveniently summarized by the flow sheet:—



The first reactions were carried out in a sealed tube under the best conditions for dehydrating the pinacol, with the hope that the maleic anhydride would add to the diene before it polymerized; this hope was not realized, most of the pinacol being rearranged and dehydrated to the pinacolone (III).

The *cis* form of diphenyltetrahydrophthalic acid (XIII) resulted from the addition reaction. On being heated above the melting point it lost water to give an anhydride (XIV). On fusion with potassium hydroxide, the *cis*-acid in part furnished the isomeric *trans* form, with some *o*-diphenylbenzene (XV), obviously a result of decarboxylation and dehydrogenation, and in part reversed into its components. The production of *o*-diphenylbenzene proved that a six-membered ring was formed in the addition reaction. When heated with sulphur, the acid was dehydrogenated to the aromatic diphenylphthalic acid (XVI); the anhydride of (XVI) was obtained on dehydration of the acid with acetyl chloride. On fusion with resorcinol and dehydrating agents, the anhydride gave a fluorescein-like melt which was brominated and iodinated—these reactions being only qualitatively studied since the colours were rather muddy.

2,3-Diphenylbutadiene reacted with α-naphthoquinone in boiling xylene to form the expected addition product (XVIII). This was easily dehydrogenated to 2,3-diphenylanthraquinone (XIX). Alkaline fusion of (XIX) gave the expected cleavage products, 3,4-diphenylbenzoic acid (XX), *o*-diphenylbenzene (XV), and benzoic acid.



(XVIII) (XIX)

(XX) (XV)

(XXI)

Only one equivalent of the diene added to benzoquinone; the addition product (XXI) rapidly decolourized permanganate. The diene did not appear to have reacted with acetylene, phenylacetylene, benzoylphenylacetylene, benzoylacrylic acid or sulphur dioxide.*

A comparison of 2,3- and 1,4-diphenylbutadienes is not strictly possible, since the latter is capable of geometrical isomerism, which may affect the ease and mode of addition. The most conspicuous differences are (i) the formation of a 1,4-dibromide with the 2,3-isomer, whereas the 1,4-analogue furnishes a 1,2-addition product, (ii) the addition of hydrogen bromide to the former, and (iii) the ease with which the 1,4-diene enters into the diene synthesis, a process obviously dependent on spatial configuration. In all the reactions that have been duplicated in both series, 2,3-diphenylbutadiene resembles 2,3-dimethylbutadiene.

Experimental

Of the two procedures investigated for securing the necessary acetophenone-pinacol, the one involving reduction in *i*-propanol solution in the sunlight (5, 16, p. 68) is preferred to the action of methylmagnesium iodide on benzil (10, 18, 22); the latter serves if time is an important factor. The mixed stereoisomers are dehydrated without separation. The diene did not crystallize readily from the oily mixtures that resulted in the various reactions, so it was usually detected and identified by formation of the dibromide (VI). In each instance where ambiguity was possible, the dibromide was treated with zinc, and the regenerated diene compared with an authentic specimen. The diene can be kept in the dark under nitrogen for several weeks, but otherwise it quickly becomes greasy and coloured.

2,3-Diphenylbutandiol-2,3 (I)

A one litre Pyrex flask containing a mixture of 90 gm. of acetophenone,† 850 cc. of *i*-propanol and one drop of acetic acid was inverted in sunlight for several months, the solvent removed *in vacuo*, and the residual oil allowed to stand; a 66% yield of the mixture (m.p. 83 to 114° C.) of pinacols slowly crystallized. It was recrystallized from a 5 : 1 mixture of benzene and petroleum ether (30 to 60° C.). The nature of the residual oil was not determined; it did not give carbonyl derivatives nor a solid dibromide, but evolved hydrogen bromide on treatment with bromine.

2,3-Diphenylbutadiene (II)

To 35 gm. of acetophenone-pinacol containing a trace (0.02 ± gm.) of phenyl-β-naphthylamine, in a brominating flask, was slowly added 105 cc. of acetyl bromide. When the vigorous reaction was over, the excess halide was removed under reduced pressure and the cooled residue cautiously neutralized with aqueous sodium carbonate. The insoluble, oily precipitate (m.p. 69 to 73° C.) was filtered and dissolved in hot alcohol; on dilution to incipient cloudiness and cooling, a 30% yield of the diene (m.p. 45 to 47° C.) separated. Instead of isolating this crude product, it is preferable to take it up in chloroform, dry the solution with calcium chloride, and convert it into the dibromide by addition of a chloroform solution of bromine. After evaporation of the solvent, a hexane wash left 17.7 gm. (33.5%) of dibromide, m.p. 144 to 147° C.

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* *Backer (2) described a sulphone, formed in a yield of 90% by heating the diene and sulphur dioxide in a sealed tube.*

† *A generous supply of this ketone was donated by Compagnie Parento, Limited.*

To secure the diene from the dibromide, to 15 gm. of the latter in 50 cc. of acetone was gradually added 7 gm. of zinc dust; when the vigorous action had subsided, the whole was refluxed for two hours, filtered hot, and evaporated to dryness. The residue was taken up in hot alcohol and water added to incipient cloudiness; on chilling in a freezing mixture, 7.8 gm. (92%) of the diene, m.p. 46 to 47° C., was obtained. Acetyl chloride was without effect (cf. ref. 21).

Johlin's sealed tube procedure (10) also gave a 30% yield of the diene *if* phenyl-β-naphthylamine or copper acetate was added to the reaction mixture; a considerable quantity of polymer resulted in every run. In the absence of these added antioxidants the yields were erratic, mostly the pinacoline (III), resulting by rearrangement of the glycol, being obtained; after analysis it was identified by its melting point and the melting point of its oxime, 151° C. (18). The diene from these runs melted at 47 to 48° C.

The polymer, left behind in the steam distillation, gradually hardened to a dark wax, softening at about 40° C. On vacuum distillation of the soft polymer it gave half its weight of a liquid (b.p. 140 to 170° C. at 20 mm.) from which were separated a little acetophenone (2,4-dinitrophenylhydrazone, m.p. 233 to 234° C.) and an oil which with bromine formed a dibromide (IV) identical with that obtained from *trans*-dimethylstilbene. The oil, thus, contains dimethylstilbene.

When maleic anhydride in acetic anhydride was used as the dehydrating agent, a trace of the addition product and a little of the acid (XIII) were isolated, but most of the diol rearranged to the pinacolone; maleic anhydride alone had no effect. The mixed anhydrides at room temperature, after four months, gave a 20% yield of the acid. Chloroacetic anhydride gave only the pinacolone.

Addition Reactions of 2,3-Diphenylbutadiene

(a) The Bromides

(1) *Addition of Bromine; 2,3-Diphenyl-1,4-dibromobutene-2 (VI).* A chloroform solution of 2,3-diphenylbutadiene was treated with bromine in chloroform until the colour persisted after shaking; heat was evolved and towards the end of the addition hydrogen bromide was evolved. The solvent was evaporated, and the residue was recrystallized from acetone. It formed long prisms, m.p. 145 to 147° C. with decomposition. It could be recrystallized from dilute alcohol without appreciable decomposition. Calcd. for $C_{16}H_{14}Br_2$: C, 52.5; H, 3 9; Br, 43.7%. Found: C, 52.5; H, 3.8; Br, 43.9%. The same dibromide was secured by following Stobbe's procedure exactly (20, p. 300).

When dissolved in acetone and refluxed with an excess of zinc dust for two hours, the diene separated practically quantitatively from the filtered solution.

It slowly gave a precipitate of silver bromide with hot alcoholic silver nitrate. It very slowly decolorized permanganate in acetone, and very slowly liberated iodine from an acetic acid solution of potassium iodide. It was unaffected by distilling a solution in acetyl bromide.

Ozonolysis. A carbon tetrachloride solution of 2 gm. of the dibromide was ozonized at 0° C. for three hours. On decomposition by water 0.2 gm. of a lachrymatory solid resulted, which was shown to be phenacyl bromide. No constituent of the remaining oil could be identified; attempts to determine the presence of formaldehyde were all negative (7, 14, 24).

(2) *Addition of Hydrogen Bromide; 2,3-Diphenyl-4-bromobutene-3 (VIII).* A solution of 2 gm. of the diene in 20 cc. of chloroform, to which a drop of ascaridole had been added, was saturated with hydrogen bromide. The mixed oil and solid that remained after removal of the solvent was triturated with hexane to remove the oil; this treatment yielded white prisms of the monobromide. After two recrystallizations from hexane, the product remained stable for several months, but otherwise soon became oily. The pure substance melted at 78° C. Calcd. for $C_{16}H_{15}Br$: Br, 27.8%. Found: Br, 27.5, 27.9%. The yield was 72% in the presence of phenyl-β-naphthylamine, 73% with ascaridole, and 62% with thiophenol. The oil which remained in the hexane was largely unchanged diene. A large-sized run (11 gm. of diene) gave 73% of monobromide, and 15% of the diene (recovered as dibromide). The residual oil almost entirely decomposed on attempted vacuum distillation. This same bromide was also easily isolated from the greasy solid left after the acetyl bromide treatment of the diol, by triturating with petroleum ether (90 to 100° C.).

Ozonolysis* gave only phenacyl bromide (mixed m.p.) and acetophenone (2,4-dinitrophenylhydrazone, mixed m.p.) but no trace of formaldehyde (9, p. 743). The bromobutene gave instantly a quantitative precipitate of silver bromide with alcoholic silver nitrate. A hot alcoholic solution deposited the diene on cooling.

3-Methyl-2-phenylindene (IX). Four grams of zinc dust was added, as fast as the violence of the reaction permitted, to 6 gm. of the bromobutene in 50 cc. of acetone, and, after refluxing for one hour, the solvent was evaporated. The crystals that separated from the residual oil were filtered and washed with acetone; the yield was 0.12 gm. (2.8%), m.p. 210° C. Calcd. for $C_{32}H_{30}$: C, 92.7; H, 7.3%; mol. wt., 414. Found: C, 92.9; H, 7.5%; mol. wt. (Rast) 384, 376. Two possibilities are a diindene and 2,3,6,7-tetraphenyloctadiene-2,6. The quantity was too small to be significant and it was not further studied. It showed a strong violet fluorescence, which favours a condensed ring formula rather than an open chain isomer.

Since the oil still contained halogen it was refluxed with more zinc an additional three hours and distilled *in vacuo*; b.p. 130° C. at 7 mm. This oil was largely the indene; the latter separated in needles from alcohol, m.p. 75 to

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* *For ozonolysis of the bromo and dinitrobutenes we are greatly indebted to Dr. G. F. Wright and Mr. A. J. Benson of the University of Toronto.*

76° C. (4). Calcd. for $C_{16}H_{14}$: C, 93.1; H, 6.9%. Found: C, 92.5; H, 6.8%. The oil contained a little diphenylbutadiene, separated and identified as the dibromide; about one gram of residue remained in the distilling flask.

(b) Reduction

The use of Adams' platinum oxide catalyst (1) gave an oil, from which a 55% yield of the solid *meso*-2,3-diphenylbutane separated. The pleasant-smelling residual oil was probably a mixture of the two isomers, since the difficultly separable *d,l*-form is reported to melt at 8° C. and have a strong odour. Stepwise reduction was not fully investigated, owing to Ott's partially completed work (15, p.2135).

Seventy-five hundredths of a gram of the diene, 0 2 gm. of catalyst, and 70 cc. of alcohol were shaken for 2.5 hr., the catalyst was filtered, and the solvent allowed to evaporate. The crystals were purified (Calcd. for $C_{16}H_{18}$: C, 91.4; H, 8.6%. Found: C, 91.5; H, 8.1%.) and found to be identical with the same hydrocarbon secured by a Wurtz reaction from α-bromoethylbenzene (below). With one equivalent of hydrogen, 0.3 gm. of the diene (0.7 gm. used) was recovered unchanged, the remainder being an anise-smelling oil that still decolorized bromine.

An alcoholic solution of the diene was unattacked by 3% sodium amalgam after five hours' refluxing, but was reduced by sodium in liquid ammonia. To a mixture of 0 3 gm. of the diene, 40 cc. of ether, and 30 cc. of ammonia was added, very slowly, 0 5 gm. of sodium in 30 cc. of ammonia; the deep blue colour decreased gradually. The solvent was removed at room temperature, with intermittent stirring—the blue colour suddenly disappeared, leaving a whitish sludge in a pale green solution. After complete evaporation, the residual jelly was boiled with alcohol saturated with carbon dioxide, filtered, and the filtrate evaporated to dryness. It was boiled with methanol, again carbonated and filtered, and evaporated to about 30 cc. The saturated hydrocarbon (VII) (high melting isomer) was filtered; further evaporation gave a second crop. The total yield was 55%. The residual oil had the same odour as mentioned above. In one instance the first crystals that separated in a very small amount were recrystallized from acetone, forming needles, m.p. 169° C. They did not decolorize bromine, and are thought to be a bimolecular reduction product (Calcd. for $C_{32}H_{34}$: C, 91.9; H, 8.2%. Found: C, 91.9; H, 8.4%).

Synthesis. The α-bromoethylbenzene was obtained by saturating 50 gm. of phenylmethylcarbinyl acetate* in 125 cc. of acetic acid with hydrogen bromide; after 48 hr., the solution was poured into 750 cc. of water, the oil that separated being removed, washed with sodium bicarbonate solution, and dried over calcium chloride. On distillation *in vacuo*, 42.2 gm. (75%) came over at 105 to 108° C. at 28 mm. It was then mixed with acetone and zinc dust added; after the vigorous reaction was over, the filtered solution was evaporated to crystallization. The solid *meso*-diphenylbutane separated from the anise-smelling oil; it was recrystallized until odourless; m.p. 122° C.

* *We are very grateful to the Compagnie Parento, Limited, for a generous supply of this ester.*

(c) Addition of Nitrogen Dioxide

2,3-Diphenyl-1,4-dinitrobutene-2 (X) and 2,3-Diphenyl-3,4-dinitrobutene-1 (XI). The gases produced by heating 40 gm. of lead nitrate were absorbed in 100 cc. of chilled hexane. This was added to a chilled solution of 6.5 gm. of diphenylbutadiene in 100 cc. of hexane; 7.5 gm. (80%) of a pale yellow solid separated. This was filtered, washed, and dried (m.p. 116 to 145° C.). It was shaken with 25 cc. of methanol, which left 3.3 gm. (35%) residue that on recrystallization from hot methanol furnished white rods, m.p. 192° C. (XI). The soluble portion was fractionally crystallized into nearly equal parts of the same substance (XI) and its isomer (X); the latter formed white needles, m.p. 151° C. Calcd. for $C_{16}H_{14}O_4N_2$: C, 64.4; H, 4.7; N, 9.4%. Found: (XI) N, 9.2; (X) C, 65.0; H, 4.8; N, 9.3%.

The high melting isomer crystallized well from benzene or chloroform, but methanol was preferred for purification. A mixture of both isomers was often encountered; it separated from dilute alcohol, with a melting point of 138° C. ± and was temporarily mistaken for a third isomer.

The high melting isomer (0.5 gm.) dissolved in 10 cc. of concentrated sodium methylate to give an orange solution; when this was added to acetic acid and diluted, the isomeric dinitrobutene (X) was precipitated. When the latter was treated in a similar manner, a yellow crystalline disodium salt separated. On acidification with acetic acid, the starting material was regenerated. Calcd. for $C_{16}H_{12}N_2O_4Na_2 . CH_3OH$: Na, 12.3%. Found: Na, 11.8, 12.0%.

Ozonolysis. This took place very slowly; from 0.2 gm. of substance (XI) in chloroform, 0.16 gm. was recovered unchanged. The aqueous layer from the decomposition was treated with dimedon, and 12 mg. (45% of theory) of the derivative of formaldehyde was obtained (9, p. 743) and identified in the usual way.

Oxidation. A mixture of 0.3 gm. of the dinitrobutene (XI), 2 gm. of potassium permanganate and 50 cc. of water was heated in a distilling flask, and the solid that steam distilled was collected and identified as benzil; there was no depression on admixture with an authentic specimen.

2,3-Diphenyl-1,4-dinitrobutadiene (XII). When the chilled solution of the disodium salt was diluted sufficiently to keep it all in solution, and bromine added dropwise until the colour persisted, a yellow solid separated. This was recrystallized from hot methanol, from which it separated in yellow rods, m.p. 184° C. with decomposition. Calcd. for $C_{16}H_{12}O_4N_2$: C, 64.9; H, 4.1; N, 9.5%. Found: C, 65.3; H, 4.2; N, 9.4%.

This was readily oxidized by potassium permanganate in hot acetone solution; the oxides of manganese were filtered and the residue, after evaporation of the solvent, boiled with alcohol and filtered hot from unoxidized starting material. On cooling, the alcohol deposited benzil, identified in the usual manner.

A preliminary repetition of Wieland's addition of nitrogen dioxide to 1,4-diphenylbutadiene gave the 1,4-dinitrobutene with the properties described (25, 26).

(d) Coupling

To a mechanically stirred clear solution of 30 cc. of concentrated sulphuric acid, 10.5 cc. of water and 3 gm. of sodium nitrite (added to acid in two equal portions) below 10° C. was added dropwise 1.8 gm. of 2,4-dinitroaniline in 15 cc. of pyridine; after two hours, 1 gm. of sulphamic acid was introduced, followed by 2 gm. of 2,3-diphenylbutadiene in 15 cc. of pyridine (6, 13). The solution became red. After a few minutes, ice was added and finally considerable water; 1.65 gm. of unchanged diene separated and was recovered. The dye was extracted from the filtrate with chloroform, and precipitated by addition of petroleum ether (90 to 100° C.). The dark red solid had an unsatisfactory melting point (166 to 168° C.; decomposition at 230° ±) and could not be recrystallized. The yield was 0.35 gm., 55%. Calcd. for $C_{22}H_{16}O_4N_4$: N, 14.0%. Found: N, 12.1%.

In a similar fashion, but without pyridine (19), the diene dissolved in glacial acetic acid was coupled with diazotized picramide. A dull yellow solid was precipitated from the greenish solution and extracted with chloroform; it did not melt below 360° C., and charred on further heating.

(e) The Diene Synthesis

(1) *cis-4,5-Diphenyltetrahydrophthalic acid (XIII).* After refluxing 9 gm. of the diene, 5.5 gm. of maleic anhydride, and 100 cc. of benzene overnight, the acidic portion was extracted from any unreacted hydrocarbon with aqueous sodium hydroxide. On adding the latter to concentrated hydrochloric acid, 12.5 gm. (94%) of an ether-soluble acid was precipitated, which, after several recrystallizations from dilute alcohol or dilute acetic acid, melted at 193° C. Calcd. for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6%. Found: C, 74.9; H, 5.8%. Calcd. for $C_{20}H_{16}O_4Ag_2$: Ag, 40.3%. Found: Ag, 40.4%. This acid is quite soluble in the usual organic solvents except petroleum fractions.

This acid was also obtained in a 20% yield by allowing a mixture of 6 gm. of the pinacol, 11 gm. of maleic anhydride, and 16 cc. of acetic anhydride to stand at room temperature for four months. The anhydride of this acid was obtained in an impure state on long standing of the diene and maleic anhydride in xylene, from the acid by refluxing with acetyl chloride, or, preferably, by heating the acid just above its melting point as long as water was evolved; after recrystallization from benzene-hexane mixture it melted at 164° C. On fusion with resorcinol and a dehydrating agent, a fluorescent solution was obtained; the dye was brominated to give a dull red-brown dye. Calcd. for $C_{20}H_{16}O_3$: C, 78.9; H, 5.3%. Found: C, 79.2; H, 5.3%.

(2) *trans-4,5-Diphenyltetrahydrophthalic acid (XIII).* When the *cis* acid was fused with potassium hydroxide at 310° C. as long as gas was evolved, the melt dissolved in water, and the solution extracted with benzene, the *trans* isomer was isolated after acidification. It separated from dilute methanol or

acetic acid in needles, m.p. 228° C. Calcd. for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6%. Found: C, 74.4, 74.6; H, 5.6, 5.7%.

The benzene extract, mentioned above, was evaporated and the residue treated with methyl alcohol; *o*-diphenylbenzene was obtained—a mixed melting point with an authentic specimen was not depressed.

(3) *3,4-Diphenylphthalic Acid (XVI).* A mixture of 3.4 gm. of the tetrahydro acid and 2 gm. of sulphur was melted at 200° C. for 16 hr. in a current of nitrogen; the evolved hydrogen sulphide was collected in aqueous silver nitrate, 3 gm. (30%) of silver sulphide being obtained. The cooled melt was extracted with aqueous sodium carbonate, the extract decolorized by Norit, and acidified with dilute sulphuric acid. The acid, 0.9 gm. (27%) recrystallized from methanol or benzene in rods, m.p. 205 to 206° C. with gas evolution. Calcd. for $C_{20}H_{14}O_4$: C, 75.5; H, 4.4%. Found: C, 75.4; H, 4.5%.

When boiled for a few minutes with acetyl chloride it furnished the corresponding anhydride, which formed prisms when recrystallized from benzene-hexane, m.p. 102° C. Calcd. for $C_{20}H_{12}O_3$: C, 80.0; H, 4.0%. Found: C, 79.6; H, 4.0%.

The same acid (XVI) was secured in small amounts by heating a mixture of the diene and acetylene dicarboxylic ester at 180 to 190° C. until it was a deep brown, extracting with alkali and acidifying the alkaline solution, and also from 3,4-diphenylfuran and maleic anhydride by the usual procedure of saturating an acetic acid solution of the addition product with hydrogen bromide (23).

(4) *2,3-Diphenylanthraquinone (XIX) and related substances.* A solution of 6 gm. of α-naphthoquinone and 8 gm. of 2,3-diphenylbutadiene in 100 cc. of xylene was refluxed for 2.5 hr. and left overnight. The solution was filtered from a trace of brownish sludge and the solvent removed *in vacuo.* The residue was recrystallized from 50 cc. of acetone; this afforded 10.4 gm. of a white addition product (XVIII), which was recrystallized from methanol. It formed needles m.p. 175 to 176° C. Calcd. for $C_{26}H_{20}O_2$: C, 85.8; H, 5.5%. Found: C, 85.6; H, 5.7%.

This substance gave a red solution with alcoholic potash; when air was bubbled through, the 2,3-diphenylanthraquinone (XIX) slowly separated in a yield of 90%. It crystallized from acetic acid in yellow needles, m.p. 211 to 212° C. Calcd. for $C_{26}H_{16}O_2$: C, 86.7; H. 4.4%. Found: C, 87.1; H, 4.4%.

This quinone dissolved to a brown solution in concd. sulphuric acid from which it was recovered unchanged on dilution. In very dilute methyl alcohol, sodium hydrosulphite gave a green colour; addition of sodium perborate or acid regenerated the quinone. A red colour was produced by the use of zinc and sodium hydroxide; acidification changed the colour to yellow, and aeration for several hours regenerated the quinone.

Alkaline Fusion; 3,4-Diphenylbenzoic Acid (XX). A mixture of 0.9 gm. of the quinone and 2 gm. of moist potassium hydroxide was heated in a distilling flask at 250° C. for four hours. After the addition of 50 cc. of water, the solution was distilled; ether extraction of the distillate gave 0.045 gm. (16%) of *o*-diphenylbenzene, identified in the usual manner.

On acidification of the residual solution, a white acid was precipitated; after solution in acetic acid and decolorizing, water was added to incipient cloudiness. 3,4-Diphenylbenzoic acid separated; a second crop was obtained by further dilution. The total amounted to 0.47 gm. or 69%. It was recrystallized from acetic acid, from which it separated in prisms, m.p. 218° C. Calcd. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.1%. Found: C, 83.2; H, 5.3%. It recrystallized unchanged from acetyl chloride.

The original aqueous solution from the acidification was extracted with ether, and 0.15 gm. of benzoic acid obtained. A larger sized fusion gave 70% of (XX), 72% of benzoic acid, and 21% of *o*-diphenylbenzene.

(5) *Other Addends to Diphenylbutadiene.* Tetrahydrodiphenylnaphthoquinone (XXI) was obtained by heating 4 gm. of the hydrocarbon and 1.5 gm. of quinone in 20 cc. of benzene on the steam bath for 18 hr., and extracting unreacted diene with hexane from the residue after removal of solvent. The portion insoluble in hexane (1.6 gm.) was recrystallized from methanol, from which it separated in large pale yellow needles or rods, m.p. 163° C. Calcd. for $C_{22}H_{18}O_2$: C, 84.1; H, 5.8%. Found: C, 84.4; H, 5.7%.

There was no detectable addition of acetylene, β-benzoylacrylic acid, phenylacetylene, benzoylphenylacetylene or sulphur dioxide.

(*f*) *The Bromination of the Dimethylstilbenes*

2,3-Diphenyl-2,3-dibromobutanes (IV). The *cis* and *trans* forms of dimethylstilbene were brominated in chloroform using 1 gm. of the hydrocarbon, 1.6 gm. of bromine, and 20 cc. of chloroform. The *trans* form gave 1.2 gm. of a dibromide that separated from hexane in needles, m.p. 149 to 152° C. When mixed with the dibromide (VI) from the diene, the melting point was depressed 10° C. The *cis* form gave a product that separated in diamond-shaped prisms, m.p. 142 to 144° C. with decomposition; mixtures with the dibromide from the *trans* form were depressed 10° C.

Both dibromides were unstable in alcoholic solutions, in contrast to the 1,4-dibromide (VI), giving oils. On refluxing in acetone solution with zinc dust for one-half hour, filtering, and concentrating to crystallization, both dibromides gave *cis*-dimethylstilbene, as shown by comparison with authentic specimens.

Beschke's dibromide was secured by following his procedure (3, pp. 120, 149), starting with *trans*-2,3-diphenylbutene-1,4-dicarboxylic acid.* A mixed melting point with the above dibromide from the *trans*-dimethylstilbene was not depressed, while that with the 1,4-dibromide from the diene was lowered 5° C.

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* *We are indebted to Mr. H. B. Yuen for the preparation of this substance.*

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXI. *CORYDALIS LUTEA* (L.) DC.[1]

By Richard H. F. Manske[2]

Abstract

Corydalis lutea (L.) DC. has yielded a total of seven alkaloids, four of which, namely: protopine, *l*-tetrahydro-palmatine, *l*-isocorypalmine, and isocorydine, are well known from other sources. The occurrence of the last, unaccompanied by corydine, is unique thus far. The name *stylopine* is retained for one of the alkaloids. On racemization it yields *dl*-tetrahydro-coptisine. *Ochrobirine* (alkaloid F14), one of the constituents, contains an esterifiable non-phenolic hydroxyl group, and the suggestion is advanced that it may be 13-hydroxy-protopine. Finally, a new non-phenolic alkaloid for which the name *luteanine* (alkaloid F44) is proposed, was found. It is isomeric with cularine, $C_{20}H_{23}O_4N$, and, like the latter, contains three methoxyl groups and an indifferent oxygen atom. It is pointed out that the nature of the chemical constituents, in this case alkaloids, offers a possible means of determining interrelations within a family. The close relation between *C. lutea*, *C. claviculata*, and *C. ochroleuca*, which has been proposed on morphological grounds, is not evidenced in the alkaloid constituents.

It is becoming increasingly evident that the chemical examination of plants offers a means of resolving disputed points of taxonomy. There are two important obstacles to classification based on morphology alone. In limiting cases, difficulties arise in closely related species, and botanists have no generally accepted criteria that would serve to allocate specificity to plants that are frequently regarded as varieties of a given species. In a previous communication the author has adduced evidence which, in his opinion, is sufficient to warrant the deduction that *C. micrantha* is not to be regarded as a varietal form of *C. aurea*. Similarly, *C. crystallina*, on the basis of chemical examination, is regarded as more closely allied to *C. sempervirens* than to *C. aurea*, of which it has been regarded as var. *crystallina* Torr. et Gray (10). A second moot point arises in attempts to subdivide a genus into sections and subsections. In this connection the three plants *Corydalis claviculata* (L.) DC., *C. lutea* (L.) DC., and *C. ochroleuca* Koch, have been grouped together in the section Stylotome Prantl., albeit, the first is differentiated from the others chiefly on account of ill-developed tendrils terminal on the leaves. *C. claviculata* has been under investigation for some time, but great difficulties have been encountered in the crystallization of most of the fractions. Nevertheless, the results thus far obtained do not justify the assumption of more than a remote relation. In fact, only two alkaloids, one of which is protopine, are contained in both plants. In the case of *C. ochroleuca** the relation to *C. lutea* is admittedly close. Of a total of eleven alkaloids in both plants, four are common constituents (protopine, ochrobirine (F14), *l*-isocorypalmine, and stylopine). Nevertheless, such typical alkaloids as isocorydine (*C. lutea*) and bicuculline (*C. ochroleuca*) serve to differentiate rather sharply two species that occasionally grow side by side but apparently do not hybridize. It is pertinent to note here that, while both the aporphine and phthalide-isoquinoline bases are widely distributed, no case is as yet known in which both types occur in the same plant, and a general system of classification based upon such considerations may well bear a close relation to a natural one. A similar and strictly parallel case is found in the pair, *Dicentra canadensis* and *D. cucullaria* (4, 6). Aporphine alkaloids (corydine, isocorydine, and bulbocapnine) occur only in the former and phthalide-isoquinoline alkaloids (bicuculline and corlumine) occur only in the latter. Nevertheless both have been relegated to the section Cucullaria Raf.** It is significant that the widespread protoberberine alkaloids are lacking in the above two species of *Dicentra* but occur in diverse forms in the three species of *Corydalis* mentioned above.

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In addition to the alkaloids already mentioned (protopine, ochrobirine, *l*-isocorypalmine, *l*-tetrahydro-palmatine, and isocorydine), *C. lutea* has yielded two alkaloids, one of which has been identified as stylopine an alkaloid first isolated from *Stylophorum diphyllum* by Schlotterbeck and Watkins (11). The author prepared a specimen of stylopine from the same source. It melts at 202° C.† and a mixture with a specimen from *C. lutea* melting at 206° C. melted at 204° C. The difference in melting points of the two bases has been found to be due to the presence of an appreciable quantity of the *dl*-base in the higher melting form. Go (3) has made the suggestion that the *l*-tetrahydro-coptisine which he isolated from *C. ternata* is identical with stylopine, and this suggestion is now proved to be correct. In the interests of priority and simplicity it is proposed to retain the name stylopine. The partially racemic stylopine from *C. lutea* was oxidized with iodine to the quaternary iodide (coptisine iodide) and the latter reduced to the tetrahydrobase. It melted at 221° C. and proved to be identical with the *dl*-tetrahydrocoptisine obtained by the author from *Fumaria officinalis* (8). A mixture of the pure *dl*-base with stylopine melted rather indefinitely at 210 to 215° C.

The remaining base, now termed *luteanine* (F44), is isomeric with cularine, $C_{20}H_{23}O_4N$, and like the latter, contains three methoxyl groups and an indifferent fourth oxygen atom.

The presence of isocorydine in the plant under consideration is of interest in that it has hitherto been found only in two plants (2, 4) and then only in association with corydine. *Ochrobirine* is the name now given to alkaloid F14 first obtained from *C. sibirica* (5). It has been observed that it yields a basic crystalline mono-acetyl derivative; hence, one of the oxygen atoms is probably present in an aliphatic hydroxyl group. Since the colour reaction is that of the protopine alkaloids and since at least one example is on record in which a hydroxyl group is a substituent in the heterocyclic system (9), the tentative suggestion that ochrobirine is 13-hydroxy-protopine is an attractive one. Some confirmation of such a structure was obtained when it was observed that a small amount of cuprous oxide is formed when ochrobirine is boiled with Fehling's solution containing some alcohol to render it soluble.

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* *See the following paper.*

** *It is of interest to note that Pursh (Fl. Amer. Sept. II, 462 (1814).) has suggested a new generic name, Perizomanthus, for Dicentra cucullaria.*

† *All melting points are corrected.*

With reference to *l*-isocorypalmine, it may now be stated with some certainty that the identification is correct. It was first encountered in *C. caseana* (7), and was termed casealutine (F32). Methylation yielded an alkaloid that has now been identified with *l*-tetrahydro-palmatine. The melting point *in vacuo* is 240° C. without appreciable decomposition, and this is the value recorded by Gadamer and co-workers (1).

Experimental

The material for the present investigation was grown in a local garden and collected in September when it was still in flower although some seed had ripened. Representative specimens were sent to the Royal Botanic Garden, Kew, England, for identification. The author is pleased to acknowledge his indebtedness to the Director, Sir Arthur Hill, and to Mr. H. W. Pugsley for their kind attention to this detail. There was available a total of 6.6 kilos of dried material of which the roots constituted only an insignificant portion.

The following is a summary of the isolated alkaloids and the fractions from which they were isolated.

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,—*l*-tetrahydro-palmatine, *l*-stylopine, luteanine.
EC—Phenolic bases extracted from alkaline solution by means of ether,—isocorydine.
BCE and EEC—Phenolic bases precipitated by carbon dioxide,—*l*-isocorypalmine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform.

BS—Non-phenolic bases,—protopine, ochrobirine.
BSE and EES—Phenolic bases precipitated by carbon dioxide,—(not crystallized).

Luteanine

The fraction (BC) was redissolved in dilute hydrochloric acid, the clear filtered solution basified with ammonia, and the liberated bases were extracted with ether. The extract was clarified by means of charcoal and evaporated somewhat; colourless stout prisms crystallized from the solution. As thus obtained the base melted at 178° C. It was recrystallized twice from ether, in which it is only sparingly soluble. *Luteanine* thus obtained melted at 183° C. Recrystallization from methanol yielded stout colourless prisms of the same melting point. The yield was 0.09%. Found: C, 70.33, 70.40; H, 6.79, 6.78; N, 4.26, 4.20; OMe, 27.71, 27.63%. Calcd. for $C_{20}H_{23}O_4N$: C, 70.38; H, 6.75; N, 4.10; 3OMe, 27.27%.

l-Tetrahydro-palmatine and l-Stylopine

When the mother liquor from the first crop of luteanine was evaporated to a small volume a mixture of bases crystallized. The more soluble portion was removed by washing with ether. The residue consisted largely of luteanine. The extract was evaporated to a small volume and on cooling deposited *l*-tetrahydro-palmatine, which, either alone or in admixture with an authentic specimen, melted at 141° C. A further amount of the same base was obtained from the mother liquor as its sparingly soluble hydrochloride. A total of 0.2% was obtained. The aqueous mother liquor from the latter was basified with potassium hydroxide and the liberated bases were extracted with ether. Evaporation of the solvent yielded a mixture from which the readily soluble *l*-tetrahydro-palmatine was separated by extraction with methanol. The sparingly soluble residue was recrystallized twice from chloroform-methanol and obtained in pale yellow fine prisms melting at 206° C. When this base was admixed with a specimen of *l*-stylopine (m.p. 202° C.) prepared from *Stylophorum diphyllum*, the mixture melted at 204 to 205° C. $[\alpha]_D^{23} = -178°$ ($c = 0.8$ in chloroform). The yield was somewhat less than 0 01%. Found: C, 70.14, 70.14; H, 5 30, 5.36; N, 4.49, 4.63%; OMe negative. Calcd. for $C_{19}H_{17}O_4N$: C, 70.59; H, 5.26; N, 4 33%.

That the base in reality is a partially racemic *l*-stylopine was proved by completely racemizing a portion of it. For this purpose 0 2 gm. was dissolved in 100 cc. boiling ethanol containing 2 gm. sodium acetate. Iodine was added to the boiling solution until an excess was present. The mixture was cooled and the dark brown quaternary iodide (coptisine iodide) was filtered off and washed with ethanol. It was suspended in glacial acetic acid to which some hydrochloric acid had been added. Zinc dust was added to the boiling solution until the mixture was colourless. Water was added, the filtered solution basified with excess ammonia, and the liberated base extracted with ether. The ethereal solution was thoroughly washed with water and evaporated to dryness. The resinous base crystallized at once in contact with methanol. It was recrystallized from chloroform-methanol and the colourless fine needles thus obtained melted either alone or in admixture with a specimen of *dl*-tetrahydro-coptisine at 221° C.

Isocorydine

The fraction (EC), as obtained by ether extraction from the strongly alkaline solution, consisted of almost pure isocorydine. When recrystallized twice from hot methanol it was obtained in large pale yellow prisms melting sharply at 184° C., and admixture with an authentic specimen did not lower the melting point. Yield, 0.07%.

An examination of the mother liquor from the latter failed to reveal the presence of corydine, for which a special search was made. In view of the sparing solubility of the hydrochloride of this base and the failure to obtain it, the conclusion that corydine is not present is a reasonable one.

l-Isocorypalmine

The fraction (EEC) crystallized with great facility in contact with methanol, and fraction (BCE) crystallized readily when its solution in chloroform was evaporated somewhat and treated with methanol. The bases from these fractions proved to be identical. Further purification was effected by recrystallization from chloroform. *l*-Isocorypalmine as thus obtained melted at 230° C. Gadamer, Späth, and Mosettig (1), who isolated the *d*-form of this base from *C. cava*, give the melting point as 239° C., presumably uncorrected *in vacuo*. The base here described melted at 240° C. *in vacuo*. The optical rotation is $[\alpha]_D^{27} = -303°$ ($c = 0.4$ in chloroform). In admixture with a specimen of the alkaloid previously described as casealutine (7) there was no observable depression of the melting point, either in an open melting point tube or *in vacuo*. The methyl ether proved to be identical with *l*-tetrahydropalmatine. The yield of *l*-isocorypalmine was 0.01%.

Protopine and Ochrobirine

The fraction (BS) consisted of only a small amount of bases. Nevertheless, the isolation of pure protopine in a yield of 0.02% was readily effected by crystallization from chloroform-methanol.

The mother liquor from the crystallization of the protopine was evaporated to dryness and the residue dissolved in dilute hydrochloric acid. The filtered solution was basified with potassium hydroxide and extracted with ether. The washed solution was freed from solvent and the residue dissolved in a small volume of methanol. A base crystallizing in fine colourless needles was thus obtained. It melted at 138 to 139° C. with the evolution of a gas. This is the behaviour of the methanolate of alkaloid F14 (K), first obtained from *C. sibirica* (5), and a mixture of the two melted at 139° C.

It has been found that this alkaloid, for which the name *ochrobirine* is proposed, can be obtained free from solvent of crystallization if it is recrystallized from dry benzene. It is then obtained in hard stout polyhedra that melt at 198° C. Specimens from both sources were obtained in this form and admixture of the two did not lower the melting point. The solvent-free base yielded the following analytical figures. Found: C, 64.65, 65.39, 65.36; H, 5.20, 5.11, 5.37; N, 3.99, 4.05%; OMe, negative. Calcd. for $C_{20}H_{19}O_6N$: C, 65.04; H, 5.15; N, 3.79%.

The analytical figures previously recorded are for the mono-methanolate, and they agree as well for $C_{20}H_{19}O_6N \cdot CH_3OH$ as for the formula given earlier.

When the non-solvated base is dissolved in a small volume of chloroform and the solution treated with methanol, the fine needles of the methanolate, melting not quite sharply at 139° C., are again obtained. In chloroform ($c = 0.4$) the optical rotation was $[\alpha]_D^{21} = +35.9°$.

Acetyl-ochrobirine

The non-solvated form of ochrobirine (0.1 gm.) was heated with acetic anhydride (0.6 gm.) on the steam bath for 60 min. The cooled mixture was diluted with water and, after the excess anhydride was hydrolyzed, sodium carbonate was added. The precipitated base was filtered off, washed, and dried. It was recrystallized from hot methanol, in which it is readily soluble. Fine colourless needles melting sharply at 177° C. were thus obtained. *Acetyl-ochrobirine* yields with sulphuric acid an orange coloured solution, which changes to pink, slowly at room temperature and rapidly on warming. Further heating yields a deep purple solution. Calcd. for $C_{22}H_{21}O_7N$: C, 64.23; H, 5.11; N, 3.41%. Found: C, 63.64, 63.62; H, 5.20, 5.35; N, 3.16, 3.24%.

An attempt to reduce ochrobirine with zinc amalgam and diluted hydrochloric acid yielded an isomeric base. It was isolated from the basified solution by extracting with ether and adding methanol to the greatly concentrated solution. When recrystallized from chloroform-methanol it was obtained in colourless prisms melting at 238° C. The colour reaction with sulphuric acid was the same as that of ochrobirine, and it is possible that the attempted reduction merely effected racemization. Found: C, 64.95; H, 5.19; N, 3.60%. Calcd. for $C_{20}H_{19}O_6N$: C, 65.04; H, 5.15; N, 3.79%.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXII. *CORYDALIS OCHROLEUCA* KOCH[1]

By Richard H. F. Manske[2]

Abstract

Eight alkaloids have been isolated from *Corydalis ochroleuca* Koch. Of these, six, namely, protopine, ochrobirine, *l*-tetrahydro-palmatine, bicuculline, *l*-corypalmine, and *l*-isocorypalmine, have been described from other sources. The last was the most abundant of the alkaloids in this plant, and was isolated in 0.11% yield of the dry weight. Two apparently new alkaloids have also been found. They are referred to as *alkaloid F45* ($C_{20}H_{19}O_8N$) and *alkaloid F46* ($C_{11}H_9O_2N\ .\ \frac{1}{2}H_2O$). The former is phenolic and the latter contains a methylenedioxy group.

In a previous paper (2) the author pointed out that, on the basis of taxonomic classification, *Corydalis claviculata* (L.) DC., *C. lutea* (L.) DC., and *C. ochroleuca* Koch are regarded as closely related and therefore placed in one section, namely, Stylotome Prantl. It may be pointed out that, as the name indicates, *C. ochroleuca* can be distinguished from *C. lutea* by virtue of the fact that its flowers are white and yellow, whereas those of the latter are pure yellow. Closer examination reveals the fact that the axillary angles in *C. ochroleuca* are much more acute than those of *C. lutea*, which tend to approach right angles. These features are clearly shown in the accompanying plate, in which *C. claviculata* is included for comparison. In general aspect the last is obviously different from the others, but this is largely due to its more branched and climbing habit.

The chemical relation between *C. lutea* and *C. ochroleuca* has already been discussed, and the present paper deals with the alkaloids that have been isolated from the latter plant. Of a total of eight alkaloids only two appear to be new and are referred to as alkaloids F45 and F46. Both bases lack methoxyl groups and the former appears to be phenolic. Alkaloid F45 yields analytical figures in agreement with the empirical formula $C_{20}H_{19}O_8N$. In view of its solubility in bicarbonate solutions and insolubility in ether, it may be the hydroxy-acid form of a phthalide-isoquinoline alkaloid containing an additional hydroxyl group in the benzene ring. Alkaloid F46 is best represented by $C_{11}H_9O_2N\ .\ \frac{1}{2}H_2O$. It is expected that more material will be available in the near future, and the further characterization of these alkaloids will then be attempted.

The remaining alkaloids, namely, *l*-tetrahydro-palmatine, bicuculline, *l*-corypalmine, *l*-isocorypalmine, protopine, and ochrobirine, have been frequently described and call for no special comment, except that this is the third recorded source of the last. Finally, at the risk of weary repetition, it is again pointed out that the chemical examinations reported in this series

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[2] *Chemist, National Research Laboratories, Ottawa.*

cannot be regarded as complete. Paucity of material and difficulties of crystallization are obstacles not immediately surmountable.

Experimental

There was available a total of 5.8 kg. of dried and ground material. The plants were grown in a local garden in a plot adjacent to that in which *C. lutea* was grown. Several specimens were sent to the Royal Botanic Garden, Kew, England, for identification, and the author records his indebtedness to Sir Arthur Hill, the Director, for his valuable aid.

The following is a summary of the alkaloids together with the fractions from which they were isolated.

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,—*l*-tetrahydro-palmatine, bicuculline.
EC—Phenolic bases extracted from alkaline solution by means of ether,—*l*-isocorypalmine.
BCE and EEC—Phenolic bases precipitated by carbon dioxide,—*l*-corypalmine.
CEC—Phenolic bases extracted from the carbonated solution by means of chloroform,—alkaloid F45.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—protopine, ochrobirine.
ES—Phenolic bases extracted from alkaline solution by means of ether,—alkaloid F46.
BSE and EES—Phenolic bases precipitated by carbon dioxide,—*l*-isocorypalmine (trace).

Bicuculline and l-Tetrahydro-palmatine

A solution of fraction (BC) in methanol was partly neutralized with hydrochloric acid and treated with a little ether. A small amount of crystalline material separated from this mixture. After two recrystallizations from chloroform-methanol it was obtained in colourless prisms melting at 177° C.*, either alone or in admixture with a specimen of bicuculline. A portion was converted into the high melting form (m.p. 195° C.); admixture of this with bicuculline did not lower the melting point. The yield was 1.5 gm.

The filtrate from the bicuculline was diluted with water and freed from organic solvents on the steam bath. The filtered solution was basified with potassium hydroxide and the liberated base extracted with ether. The washed and concentrated extract deposited the hydrate of *l*-tetrahydro-palmatine on cooling. It melted with effervescence at 115° C. A portion was converted to the anhydrous form, which melted at 142° C. either alone or in admixture with an authentic specimen. The yield was 2.1 gm.

l-Isocorypalmine

During the extraction of the alkaline filtrate from fraction (BC) to obtain fraction (EC), small amounts of dilute hydrochloric acid were added to reduce the alkalinity. While the filtrate was still quite alkaline, a crystalline preci-

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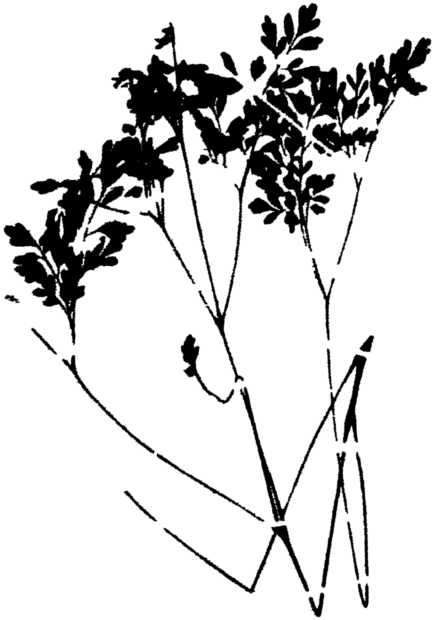
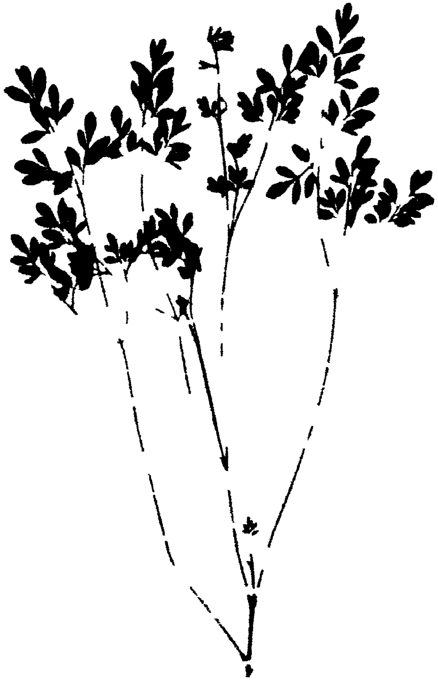
* *All melting points are corrected.*

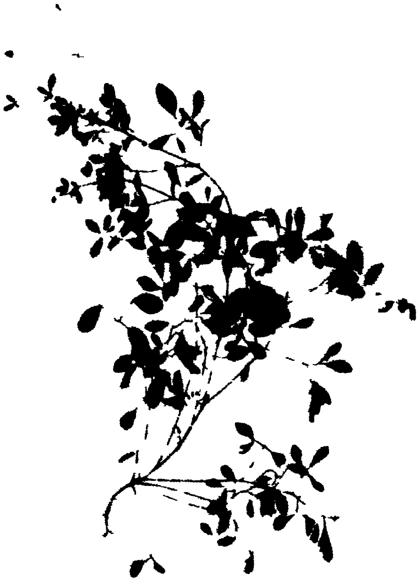
PLATE I



Corydalis ochroleuca



Corydalis lutea



Corydalis claviculata

pitate virtually insoluble in ether separated from the mixture. It was filtered off, and, after washing and drying, it melted at 231° C. to a reddish-brown melt. It was recrystallized from a large volume of hot chloroform in which it is only sparingly soluble. It still melted at 231° C. *In vacuo* it melted more sharply at 240° C. Also, in admixture with specimens of *l*-isocorypalmine from *C. lutea* (2) and *C. caseana*, it melted at 240° C. *in vacuo*. The ether extract (EC) consisted largely of the same base. The total yield was 6.7 gm. (0.11%). *l*-Isocorypalmine is therefore the principal alkaloid in *C. ochroleuca*, which plant incidentally is by far the best source of this hitherto rare alkaloid.

l-Corypalmine

The fractions (BCE and EEC) in contact with methanol yielded a further small amount of *l*-isocorypalmine, which crystallized readily. The filtrate from this alkaloid was evaporated and the residue dissolved in dilute hydrochloric acid. The bases were regenerated from the filtered solution by means of ammonia and extracted with ether. The residue from the ether extract crystallized in contact with methanol. As thus obtained it melted at 227 to 228° C. and admixture with *l*-isocorypalmine lowered the melting point to 215° C. In admixture with *l*-corypalmine it melted at 228 to 229° C. With sulphuric acid it gave a series of colours indistinguishable from those of the latter. The yield was 0.07 gm.

Alkaloid F45

The aqueous carbonated solution from which fraction (EEC) had been obtained yielded to chloroform extraction a moderate amount of another alkaloid. This fraction, for which the designation (CEC) is now proposed, is of appreciable bulk in the case of only a few plants. In the present instance the residue from the chloroform extract could not be crystallized directly. It was dissolved in dilute hydrochloric acid and the filtered solution basified with ammonia. No immediate precipitate was formed. The slightly turbid solution was filtered and allowed to evaporate slowly. The crystalline base which separated in the course of several days was filtered off and washed with water. It was dissolved in chloroform and the solvent evaporated. Methanol was added and the remaining chloroform boiled off. The cautious addition of water yielded hard colourless prisms, which were filtered off and washed with the following liquids in the order given,—methanol, water, methanol, and ether. Alkaloid F45, as thus obtained, melted to a dark tar at 268° C. It dissolves in sulphuric acid to a greenish-yellow solution that becomes orange on gentle heating. Further heating changes the colour of the solution to brown and finally to olive, which colour remains on cooling. The yield was 0.1 gm. Found: C, 60.62, 60.60; H, 4.76, 4.77; N, 3.29, 3.30%; OMe, absent. Calcd. for $C_{20}H_{19}O_8N$: C, 59.85; H, 4.74; N, 3.49%.

Protopine and Ochrobirine

The fraction (BS) was dissolved in chloroform and the filtered solution (charcoal) evaporated to dryness. The residue was dissolved in dilute hydrochloric acid and the filtered solution basified with potassium hydroxide. The liberated base was extracted with ether and the extract evaporated to dryness. A methanolic solution of the residue was inoculated with a crystal of protopine. The base which then crystallized was virtually pure protopine (yield, 0.9 gm.).

The filtrate from the protopine deposited in the course of several days a crop of colourless elongated needles, which were dissolved in boiling methanol. Ochrobirine crystallized with great facility when the methanolic solution was evaporated to a small volume. It melted at 138 to 139° C. either alone or in admixture with a specimen of alkaloid F14 from *C. sibirica* (1). A portion was converted to the high melting form (m.p. 198° C.), and this had the properties of the base similarly obtained from the alkaloid from other sources. The yield was 0.3 gm.

Alkaloid F46

The fraction (ES) crystallized with great facility when the ether was distilled off. It was dissolved in chloroform and the solvent evaporated. Crystallization ensued almost at once when the amorphous residue was dissolved in hot methanol. The base was recrystallized again from chloroform-methanol; it then consisted of large pale yellow prisms that melt without appreciable decomposition at 227° C. It dissolved in sulphuric acid to yield a pale yellow solution; when the solution was warmed the yellow colour faded somewhat, and on further heating it only became brown. A test for the methylene-dioxy group with 80% sulphuric acid and phloroglucinol was strongly positive. It is not probable that alkaloid F46 is phenolic, as it would not dissolve in aqueous potassium hydroxide solution. The yield was 0.15 gm. Found: C, 66.22, 66.26; H, 5.23, 5.40; N, 7.18, 7.26%. OMe, negative. Calcd. for $C_{11}H_9O_2N \cdot \frac{1}{2}H_2O$: C, 67.35; H, 5.10; N, 7.17%.

As in all plants of the genera *Dicentra*, *Corydalis*, and *Fumaria* thus far investigated, fumaric acid was encountered.

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THE CORROSION OF IRON ELECTRODES BY A.C. IN AQUEOUS ELECTROLYTES[1]

By J. W. Shipley[2] and G. R. Finlay[3]

Abstract

The corrosion of iron electrodes when a.c. is used was found to be a function of the composition and concentration of the electrolyte and of arcing on the electrodes. No particularly corrosive effect could be attributed to the presence of chlorides, but sulphates were found to induce corrosion. Magnesium and calcium salts inhibited corrosion even in the presence of sulphates. The addition of a soluble magnesium salt to the feed water and the operation of the generator under pressure in order to prevent arcing are suggested as a means of minimizing corrosion of the electrodes in a boiler of the resistor type.

Introduction

The preparation of steam in electric boilers of the resistor type, in which iron electrodes, natural waters as electrolyte, and a.c. as the source of thermal energy, are used, is common practice for the generation of steam where hydroelectric power is available. A previous investigation by one of us (2) draws attention to the corrosion of the electrodes in relation to current density and arcing. The present investigation concerns the corrosion of iron electrodes in relation to the composition of the electrolyte when 60 cycle 110-volt current is used. This voltage is far below that employed in the production of steam, but is nevertheless sufficiently high to produce boiling, arcing, and gas formation, the important phenomena accompanying the generation of steam in an a-c. water resistor steam generator.

The generation of steam increases the natural salt content of the water until the lowering of the electrolytic resistance makes it desirable to "bleed" the generator and run off the water of relatively low resistance. A feed water from a river or lake may have a very low salt content, but owing to evaporation the salt content increases continuously.

Experimental

In the operation of a steam generator of this type, natural waters containing various salts in different concentrations are used. This investigation concerns the observed corrosion when a.c. and certain individual salts and salt mixtures, commonly found in natural waters, are used, the concentrations employed being those likely to be encountered in actual practice. The corrosive effect of some natural waters with a mixed salt content was also studied. Table I contains the results observed when electrodes of commercial soft iron wire, cleaned with fine emery, and of 0.102 cm. diameter and 2 to 2.5 cm. long, are submerged in the electrolyte designated, and submitted to the action of a 60 cycle, 107 to 115 volt, alternating current.

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[1] *Original manuscript received September 6, 1938.*
Contribution from the Chemistry Department, University of Alberta, Edmonton, Canada.

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The loss of iron by corrosion was determined by one or more of the methods given below.

(1) Dissolving, in sulphuric acid, the particles loosened by corrosion, reducing and titrating with potassium permanganate.

(2) Determining the loss in weight of the electrodes.

(3) Drying the products of corrosion at 120° C., weighing, and calculating the iron content from the formula $Fe_3O_4 . H_2O$.

(4) Ascertaining the excess of hydrogen over that of oxygen in the evolved gases; when calculated to iron as Fe^{++}, this gave a measure of the corrosion.

The results listed in Table I were all computed from the analysis as in Method (1), except where otherwise indicated. The corrosion is calculated as though it were uniform over the surface of the electrode, and is expressed as loss of iron off the surface in centimetres per year of continuous use. The corrosion of the electrode in pitted areas would no doubt be much more rapid than that indicated by the results tabulated.

No relation between current density and corrosion could be established, as the current fluctuates violently as soon as bubbles of steam are generated

TABLE I

CORROSION OF IRON ELECTRODES BY A-C. ELECTROLYSIS

Using submerged electrodes 0.102 cm. in diameter and 2 or 2.5 cm. in length. Current; 60 cycle, 107 to 115 volts Time of run, one hour. Temperature, the boiling point of the electrolyte

Electrolyte	Corrosion results Loss of iron off surface, in cm./year	Remarks
NaOH, *N*/10	6*, 5	Arcing in both cases
$NaHCO_3$, *N*/10	2, 6, 9	Foaming and no arcing, sludge formation
Na_2CO_3, *N*/10	12, 3, 5	Sludge formation, no arcing, foaming
NaCl, *N*/10	18, 15	No arcing
NaCl, *N*	325	Arcing
$CaCl_2$, *N*/10	6, 6, 4, 0	No arcing
$CaCl_2$, *N*	90	Arcing
$MgCl_2$, *N*/10	7, 3, 0, 15, 25	Arcing in last two runs
$MgCl_2$, 1.5 *N*	180	Arcing
$MgSO_4$, *N*/10	2, 2, 0	No arcing
$MgSO_4$, *N*	12	Arcing negligible
$CaSO_4$, sat'd	0	No arcing
Na_2HPO_4, M/4	12	Electrodes coated, no arcing
Na_2SO_4, *N*/10	80†, 135, 130*, 105, 125*, 105†°	Most of these values were also checked by measurement with micrometer. No arcing.
Na_2SO_4, *N*/20	130, 110°	No arcing
Na_2SO_4, *N*/30	85*	No arcing
Na_2SO_4, *N*/50	90 (45 at 82° C.)	No arcing
$FeCl_3$, *N*/10	163°'†	pH = 1.8. No arcing
$FeSO_4$, *N*/10	35°'†	pH = 3.8. No arcing
$KMnO_4$, *M*/100	Attack not serious	Permanganate partially reduced to MnO_2. No arcing

° *Method of analysis No. 2.*

† *Method of analysis No. 3.*

* *Method of analysis No. 4.*

All not marked were calculated from the determination of iron by Method No. 1.

on the electrodes, and the distribution of current on the electrodes becomes a function of the insulating effect of the bubbles. The size, continuity, and distribution of the bubbles on the electrodes is quite irregular and varies between the electrodes. Often all the steam is generated at one electrode. Arcing on the electrodes also causes a marked fluctuation in the current, the current invariably dropping when arcing begins.

Fig. 1, compiled from some of the data included in Table I, shows more strikingly the relative rates of corrosion of iron in 0.1 *N* solutions of the salts.

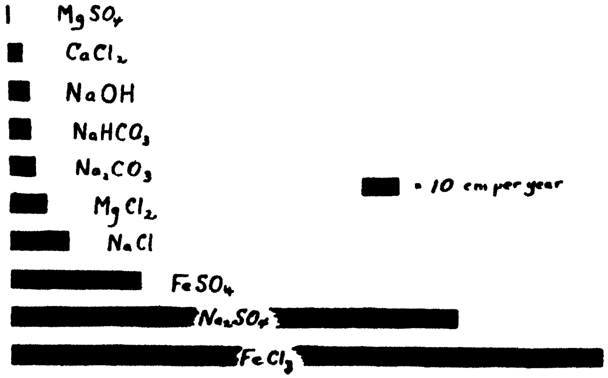

FIG. 1. *Corrosion of iron electrodes in N/10 electrolytes (a.c.)*

The figure is constructed from the average rate of corrosion in all the corresponding salt solutions.

The relative rate of corrosion was determined in some natural waters of high salt content, the concentration somewhat simulating that to be expected in an electric boiler before "bleeding" is resorted to. Five of the samples were from wells in Alberta, one was of water from a "muskeg", one from the North Saskatchewan River at Edmonton, and another a solution of "humic" or "ulmic" acid prepared synthetically from rotting moss (3). An analysis of some of these waters is given in Table II.

TABLE II

ANALYSIS OF WATERS (P.P.M.) USED IN THE CORROSION TESTS INCLUDED IN TABLE III

—	Well No. 1	Well No. 2	Well No. 3	Well No. 4	Well No. 5	Sask. River water, August
Total solids (after heating to 150° C.)	1710	1030	4954	1822	2006	199
Total hardness (Ca and Mg to $CaCO_3$)	800	500	500	20	20	152
SO_4^{--}	300	270	2300	995	400	25
Cl^-	143	24	140	77	28	4
Alkalinity (total CO_3^{--} calcd. to $CaCO_3$)	880	445	440	295	1150	110
Nature of alkalinity	Ca and Mg	Ca and Mg	Ca and Mg	Na 232, trace Ca	Na, no Mg, trace Ca	Ca and Mg
pH	8.9	7.2	8.5	8.4	9.2	8.1

The "muskeg" swamp water had a magnesium sulphate content of about 0.1 N and a pH of 6.3; the pH of the synthetic humic acid solution was 4.1.

Fig. 2 is compiled from the data in Table III.

To test whether the a-c. electrolysis of a chloride solution using iron electrodes might produce chlorine, hydrogen chloride, or hypochlorite, a series of determinations was made in which magnesium chloride was employed in concentrations varying from 0.1 to 1 *N* over a range of current densities.

TABLE III

Corrosion of iron electrodes by a-c. electrolysis (conditions as given in table I)

No arcing was observed during any of these determinations

Sample of water	Corrosion Loss of iron off surface in cm./year	pH	
		Initial	After one hour
Humic acid	0, 0*	4 1	—
"Muskeg"	0, 2†	6 3	8 0
Sask. River	0, 0, 3	8 3	9 1
Well No. 1	1, 3	8 9	> 10
Well No. 2	14, 2	7 2	8 7
Well No. 3	25, 15, 35	8 5	9 3
Well No. 4	95, 150	8 4	> 10
Well No. 5	160, 115	9 2	10

* *Electrodes coated.* † *Magnesium sulphate, about 0 1 N.*

Arcing occurred, erratic at low, but steady at higher, current densities, but no evidence of free chlorine, hydrogen chloride, or hypochlorite was found in either the residual electrolyte or in the distillate. When arcing occurred, severe corrosion was observed with the formation of the black oxide of iron. As aluminium electrodes possess a low critical current density (2) in respect to gas evolution, these were substituted for the iron electrodes, and although hydrogen and oxygen were evolved copiously no chlorine was detected. Elec-

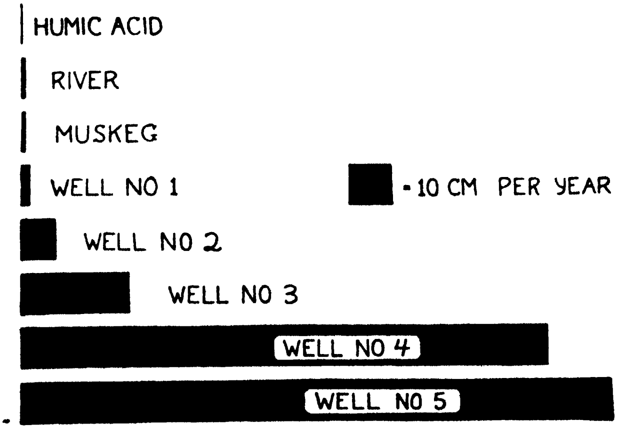

Fig. 2. *Corrosion penetration in iron electrodes—a-c. electrolysis in natural waters.*

trodes of No. 30 aluminium wire were completely corroded in three minutes. Before disintegration, the electrodes became covered with a white deposit of magnesium hydroxide, quite adherent to the electrodes, and gas evolution diminished. The pH of the electrolyte fell from 6.0 to 5.0. Gas production, principally of hydrogen and oxygen, occurred in all cases, with or without arcing, but more copiously with arcing. The excess of hydrogen over oxygen in the evolved gases gave a measure of the extent of the corrosion. Sodium hydroxide as electrolyte gave practically equivalent quantities of hydrogen and oxygen without corrosion, whereas sodium sulphate gave a large excess of hydrogen over oxygen, with a corresponding corrosion measured by the difference. Electrolytes containing calcium sulphate or magnesium sulphate evolved little gas, and the corrosion was slight. Carbonates and bicarbonates on electrolysis produced some carbon dioxide, and the pH rose from 8.5 to 10.0 whenever bicarbonate was present. Chlorides did not produce any appreciable amounts of chlorine or hydrogen chloride.

Protective Coatings

As electrolytes containing calcium and magnesium salts were observed to inhibit corrosion, tests were carried out to determine the practicability of adding substances to the electrolyte with the expectation that a measure of protection against corrosion (3) might be secured. "Water glass" was found to afford some protection when added to an electrolyte containing sulphate ions, but sludge formation and foaming were enhanced. Aluminium chloride promoted corrosion, foaming, and the production of sludge. Potassium dihydrogen phosphate inhibited corrosion in a sulphate-containing water, but, when the phosphate coated electrodes were used in the absence of phosphate, corrosion proceeded unimpeded. Apparently protection is afforded only if phosphate ions are present. Addition of lime gave no protection in an electrolyte containing sulphate ions, but calcium chloride did. A sludge of calcium sulphate was formed. Calcium chloride added to well waters Nos. 3, 4, and 5 proved to be protective unless arcing occurred. Magnesium chloride added to the well waters inhibited both the corrosion and arcing. A mixture of "water glass" and calcium or magnesium chloride was not found to be protective, and objectionable sludge formation occurred. Magnesium sulphate or chloride added to an electrolyte gave the best results, as no sludge formation followed. Sodium carbonate or sodium hydroxide did not inhibit corrosion in the presence of sulphate ions. Colloids such as glue and gelatin were ineffective.

Discussion

Reference to Tables I and III and Figs. 1 and 2 indicates that when a.c. is used there is a large difference in the rate of corrosion of an iron electrode depending on the nature of the electrolyte and the concentration. Both the cations and the anions are concerned. Production of an insoluble compound on the electrodes tends to protect the electrode from corrosion. Thus a film of calcium or magnesium hydroxide may be formed over the surface when the electrolyte contains these cations, for during the half-cycle when hydrogen is being discharged on the electrode the solution in immediate contact with the electrode possesses an excess of hydroxyl ions, and the above mentioned insoluble hydroxides may be formed. During the second half-cycle, when the electrode becomes anodic, this film may not be completely reduced, and, as electrolysis proceeds, the layer will increase and become more protective, as the underlying iron is kept from contact with the electrolyte. This explanation is supported by the experimentally observed fact that, in solutions of calcium and magnesium salts, a.c. produces on the electrodes a coating resembling these hydroxides and certainly containing the respective cations.

The formation of such protective coatings would account for the low corrosive effect of the magnesium and calcium salt electrolytes shown in Table I and Fig. 1, and also for the relative position of the natural waters, as regards corrosion, given in Table III and Fig. 2. Those waters containing either or both of these alkaline earth metals are relatively non-corrosive.

The synthetic humic acid water, although of a pH of 4.1, proved to be non-corrosive. The electrodes were covered with a visible loose deposit, probably of a colloid collected by cataphoresis.

Sodium sulphate proved to be very corrosive. Natural waters containing sulphate and little or no calcium or magnesium were also very corrosive. Sodium chloride was not particularly corrosive as compared with the sulphate, but ferric chloride was the most corrosive electroyte used. The last-named electrolyte had a pH of 1.8 and thus was quite acid; at the temperature of boiling this condition no doubt made it very reactive with the iron and kept the electrodes clear of any protective deposit.

The effect of increase in concentration of salts in the electrolyte was in general to promote arcing and corrosion. Arcing, with its consequent high temperature and the rapid formation and collapse of steam bubbles, jars the electrodes and tends to break up any loosely adhering protective coating that might form. It also increases the local current density and thus promotes corrosion.

Sodium hydroxide electrolyte was non-corrosive even when arcing occurred. Electrolysis produces hydrogen and oxygen.

Arcing on the electrode was found to be very conducive to corrosion. Since arcing occurs across bubbles of gas and the suppression of such bubbles can be secured by operating the boiler under pressure, it is suggested that generators be operated at a pressure sufficient to prevent steam formation and that the hot water be allowed to vaporize under reduced pressure in a separate chamber. The suppression of bubble formation on the electrodes would also tend to give uniform current density distribution on the surface of the electrodes and thus distribute any unavoidable corrosion uniformly over the surface. This would tend to diminish pitting of the electrode.

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THE KINETICS OF THE DECOMPOSITION REACTIONS OF THE LOWER PARAFFINS

IV. THE ROLE OF FREE RADICALS IN THE DECOMPOSITION OF *n*-BUTANE[1]

BY E. W. R. STEACIE[2] AND H. O. FOLKINS[3]

Abstract

An investigation has been made of the inhibition of free radical chain processes in the decomposition of *n*-butane by the addition of nitric oxide. The method was to initiate chains in butane at low temperatures by means of ethylene oxide, and then to investigate the efficiency of nitric oxide in suppressing these chains.

It was found that nitric oxide is not completely efficient as a chain breaker, inasmuch as sensitization by ethylene oxide persisted in the presence of large amounts of nitric oxide. It is therefore concluded that maximum inhibition of organic decomposition reactions by nitric oxide does not in all cases correspond to complete suppression of chains, and hence the real chain length in such reactions may be greater than that inferred from the results of the nitric oxide inhibition method.

Introduction

Free radicals have been detected in the high temperature thermal decomposition of the hydrocarbons by Paneth, Rice, and their co-workers [see (19)], and it has been suggested by Rice that most organic compounds, and specifically the hydrocarbons, decompose by a free-radical mechanism at lower temperatures. While the evidence in a general way supports Rice's conclusions, the specific mechanisms proposed by Rice and Herzfeld (18) have been shown in a number of cases to be untenable (15–17, 21–23, 30–33). The subject has recently been reviewed in detail (14, 28, 29), and the general aspects of the problem will therefore not be further discussed here.

In view of the importance of the question, and of the uncertainty which surrounds it, other methods of attack are of great importance. One such method which has had considerable success is the use of nitric oxide as a test for the presence of free-radical chains in organic decomposition reactions. It was found by Staveley and Hinshelwood (27) that while large amounts of added nitric oxide catalyzed many organic decomposition reactions, small amounts often caused some inhibition. They assumed that the maximum inhibition corresponds to the complete suppression of chains normally present, and thus calculated mean chain lengths of from two to twenty for a number of decomposition reactions. This is definite evidence for the presence of chains, but in most cases the chain lengths thus obtained are far too small to be in accord with the Rice-Herzfeld mechanisms. The main defect of the nitric oxide inhibition method is that the assumption that maximum

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inhibition corresponds to a complete supression of all chains is arbitrary, and makes the calculated chain lengths of somewhat doubtful significance.

A number of investigations of the paraffin decompositions have been made by this method. Staveley (26) found marked inhibition of the decomposition of ethane at 620° C. The mean chain length (defined as the ratio of the rate in the absence of nitric oxide to the lowest rate in the presence of nitric oxide) varied from 20.6 at 51 mm. ethane pressure to 6.4 at 501.5 mm. He concluded that in all probability only a few molecules decompose primarily into radicals, but that these lead to very long chains, of the order of 10^5 to 10^7 units.

A further investigation of the effect of nitric oxide on the ethane decomposition at 600° C. was made by Hobbs and Hinshelwood (11). They paid particular attention to the effect of the ethane pressure on the inhibition, and concluded that the inhibition was proportional to $1/(C_2H_6)^{0.35}$. From this they conclude that in the normal decomposition the chains are broken by recombination of radicals in the gas phase, largely with ethane molecules as third bodies. In the presence of nitric oxide the chains are assumed to end by the recombination of a radical with a nitric oxide molecule.

In a further paper (12) Hobbs and Hinshelwood compare the effect of nitric oxide on the decompositions of methane, ethane, propane, and hexane. They find that in all cases the chain length decreases with increasing pressure of the hydrocarbon. The chain lengths found vary from 3.3 to 10.1 for propane, from 1.4 to 2.3 for hexane, and from 2.9 to 4.7 for methane. They conclude that the mean chain length depends upon the relative values of three activation energies, namely, that of radical formation, of decomposition by internal rearrangement, and of chain propagation. Approximate indications are that the last tends to decrease with increasing molecular weight of the hydrocarbon.

Recently Echols and Pease (6) have reported that nitric oxide inhibits the decomposition of *n*-butane. In a later note (7) they conclude that the effect is only transient, and that nitric oxide forms an unstable compound with the chain carriers which breaks down again and gives the radicals back to the system, thus neutralizing the inhibition.

It will be apparent from the above discussion that considerable information regarding the participation of free radicals in decomposition reactions is obtainable from experiments on inhibition by nitric oxide. From a quantitative point of view, however, such experiments suffer from two defects. In the first place the assumption that maximum inhibition corresponds to the complete suppression of chains normally present is arbitrary. In the second place the chain lengths calculated are mean chain lengths, and it is left an open question whether all the decomposing molecules follow a chain mechanism, or whether very few of the primary acts involve a split into radicals but the resulting chains are very long.

Another method of investigation which has been largely used is to cause the sensitized free radical decomposition of a hydrocarbon by the addition to it of a compound which is known to give free radicals when it decomposes.

Thus in the case of *n*-butane, Heckert and Mack (36) found that sensitized decomposition occurred in the presence of decomposing ethylene oxide. Ethylene oxide has been shown to produce methyl radicals by Fletcher (8) and by Fletcher and Rollefson (9). Frey (10) also showed that 1% of dimethyl mercury could set up chains 20 molecules long in *n*-butane at 525° C. Echols and Pease (5) found also that chains were set up in *n*-butane by decomposing ethylene oxide at 425° C. By comparing the ratio of unsaturates to the carbon monoxide formed from the ethylene oxide decomposition, they calculated chain lengths as high as 12. Sickman and Rice (25) found that radicals from the decomposition of azomethane also set up a chain decomposition of *n*-butane.

It was decided that it should be possible to clear up certain of the ambiguities in the interpretation of results obtained by the nitric oxide inhibition method. An investigation has therefore been made of the efficiency of nitric oxide in breaking chains induced in *n*-butane by the addition of ethylene oxide at low temperatures where the normal decomposition of *n*-butane is negligibly slow. The advantage of this method is that under these circumstances the entire decomposition of the butane is by radical chain processes. It should thus be possible to determine unequivocally the efficiency of nitric oxide in suppressing chain processes.

Experimental

The static method was used, and the reaction was followed by observing the rate of change of pressure, and by analysis.

The apparatus was similar in principle to that used in previous investigations [see, for example (34)]. The reaction vessel, of Pyrex, had a capacity of about 600 cc., and the walls were coated with potassium chloride from a 2% aqueous solution at the beginning of the investigation. The capillary manometer was wound with nichrome wire and heated electrically to about 100° C. to prevent condensation of the reaction products. The reaction vessel was heated by an electric furnace, and the temperature was measured with a chromel-alumel thermocouple in conjunction with a potentiometer. The temperature was controlled by manual regulation, and could be maintained constant to within ±1°.

When the reaction had progressed to the desired extent, the products were collected for analysis by sudden expansion into a bulb of one litre capacity through a liquid air trap. This trap kept the pressure low in the expansion bulb, since most of the products condensed, and thus greatly increased the effective volume of the expansion bulb. Since the expansion was rapid and occurred through narrow tubing, there was no danger of fractionation through diffusion. The samples thus obtained were transferred to a Burrell gas analysis apparatus by means of a Toepler pump and a portable mercury gas holder.

n-Butane was obtained in cylinders from the Ohio Chemical and Mfg. Co., and was fractionally distilled before use. Ethylene oxide was obtained from the Eastman Kodak Co. Nitric oxide was generated by dropping mercury into a 2% solution of sodium nitrite in concentrated sulphuric acid. The resulting gas was passed over phosphorus pentoxide, and through a trap at −80° C., into a storage reservoir.

Between runs the apparatus was always kept evacuated to avoid possible complications in the acetaldehyde decomposition due to traces of oxygen (13).

Experimental Results

(A) Butane–Nitric-oxide Mixtures

A few experiments were first made on the inhibition of the decomposition of *n*-butane by nitric oxide at 525° C. The inhibiting effect was found to be considerable, in agreement with the work of Echols and Pease. Typical data are shown in Table I. The data lead to a "mean chain length" (calculated on the assumption that maximum inhibition corresponds to the complete suppression of chains) of about 16 at a butane pressure of 20 cm.

TABLE I

THE EFFECT OF NITRIC OXIDE ON THE DECOMPOSITION OF BUTANE AT 525° C.

Initial butane pressure, cm.	Initial nitric oxide pressure, cm	T_{25}, min.	Initial rate, expressed as pressure increase in mm. per min.	Relative rate
21 50	0 00	19	11 4	1 00
17 42	0 58	36	1 3	0 11
19 76	1 74	45	0 7	0 06
18 30	2 10	44	0 7	0 06

The complete data for the above runs are plotted in Fig. 1. It will be noted that the initial rate of the reaction in the presence of nitric oxide is very slow, but that in the later stages of the reaction there is little or no difference between the rates in the presence and in the absence of nitric oxide. This is in agreement with the conclusions of Echols and Pease. Maximum inhibition appears when the partial pressure of nitric oxide is about 20 mm.

The above results are given merely to show the agreement with those of previous workers. Further work is in progress on this phase of the problem, and the results will be reported in full later.

(B) Butane–Ethylene-oxide Mixtures

The effect of ethylene oxide on butane at 450° C. was next investigated. At this temperature the ordinary decomposition of butane is negligibly slow (the time to quarter value being about 160 hr.), and the sensitizing effect of ethylene oxide can be investigated without complications due to the normal

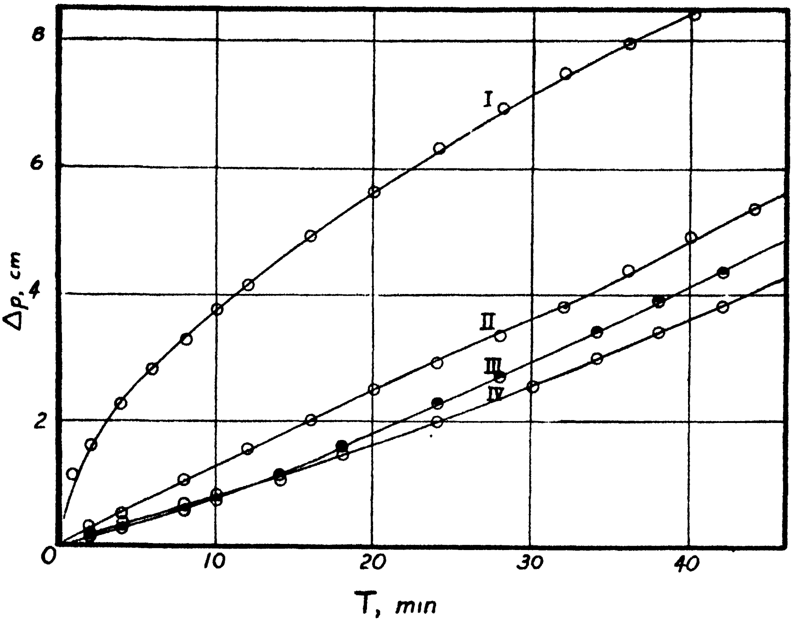

FIG. 1. *Runs at 525° C. whose initial pressures in centimetres are: Curve I. Butane, 21.50. Curve II. Butane, 17.42; NO, 0.58. Curve III. Butane, 19.76; NO, 1.74. Curve IV. Butane, 18.30; NO, 2.10.*

decomposition. Table II gives results for a series of runs made with constant ethylene oxide pressures of about 7 and 3 cm. and mixtures containing varying amounts of butane. The complete data for the experiments with an ethylene oxide pressure of 7 cm. are plotted in Fig. 2.

It will be seen that considerable sensitized decomposition of butane has occurred. A direct calculation from the data in the last column of Table II

TABLE II

THE SENSITIZED DECOMPOSITION OF BUTANE BY ETHYLENE OXIDE AT 450° C.

Initial ethylene oxide pressure, cm.	Initial butane pressure, cm.	$\frac{C_4H_{10}}{(CH_2)_2O}$, approximate ratio	Initial rate of pressure increase, mm. per min.
7.10	0.00	0 : 1	5.04
7.06	7.24	1 : 1	6.63
7.02	13.98	2 : 1	9.66
7.00	27.30	4 : 1	15.0
6.95	52.55	8 : 1	20.4
2.84	0.00	0 : 1	2.5
2.87	2.93	1 : 1	5.4
2.80	5.95	2 : 1	7.8
3.00	12.10	4 : 1	12.3
2.84	43.06	16 : 1	23.0

would indicate that up to 10 molecules of butane are decomposed for each molecule of ethylene oxide. Actually the chain lengths must be greater than this for two reasons. In the first place, according to Fletcher and Rollefson (9) only a fraction of the ethylene oxide molecules give rise to radicals in decomposing. This will make the chain lengths higher than a direct calculation would indicate.

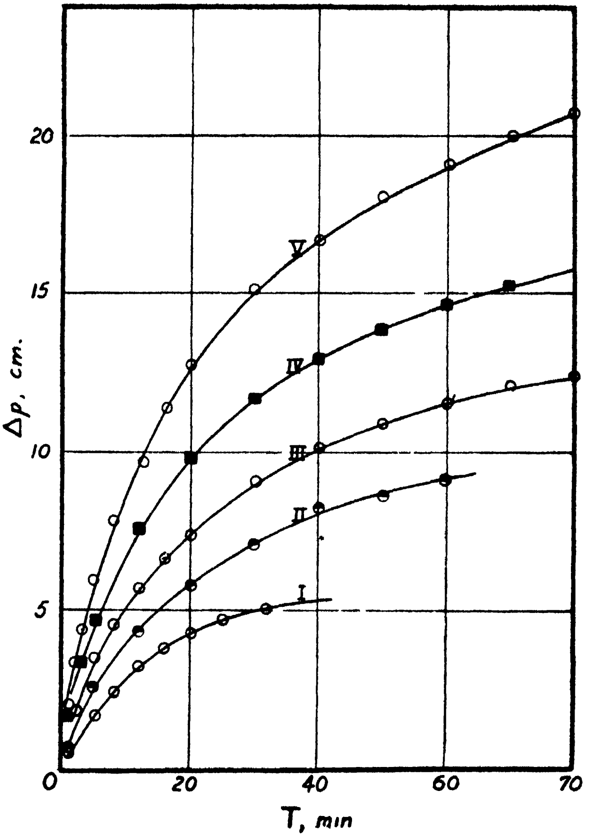

FIG. 2. *Butane–ethylene-oxide runs at 450° C. Ethylene oxide at a constant initial pressure (approx. 7 cm.)*

Curve	*I*	*II*	*III*	*IV*	*V*
Approx. ratio butane/ethylene oxide	*0 : 1*	*1 : 1*	*2 : 1*	*4 : 1*	*8 : 1*

There is also a second reason why the apparent chain length is too small. Heckert and Mack in their original work on the ethylene oxide decomposition noted that in 1 : 2.3 ethylene-oxide–butane mixtures the rate of the ethylene oxide decomposition was only about one-half that of ethylene oxide alone. It is not therefore justifiable to infer the amount of ethylene oxide decomposing in an ethylene-oxide–butane mixture from the rate of its normal decomposition. It follows that an accurate determination of the chain length can be made only by determining by analysis the relative amounts of ethylene oxide and of butane decomposed. We have, therefore, as have Echols and Pease, determined the relative amounts of carbon monoxide and of unsaturated hydrocarbons in the products, and we will use the ratio C_nH_{2n}/CO as a measure of the relative amounts decomposed. Actually, of course, the initial products are what should be determined, but in order to obtain sufficiently large samples for analysis we have determined the values of the ratio at quarter-time. The analyses were made with cuprous chloride as an absorbent for carbon monoxide, and fuming sulphuric acid for unsaturates. Fuming sulphuric acid also absorbs a little butane, but this can be corrected for by means of blank experiments with pure butane. The results of the analyses are given in Table III.

TABLE III

BUTANE–ETHYLENE-OXIDE MIXTURES AT 450° C.
ANALYSES AT T_{25}

Approximate ratio $\frac{\text{butane}}{(CH_2)_2O}$	Mole per cent		$\frac{\text{Unsaturates}}{\text{CO}}$
	Unsaturates	CO	
8	18.2	3.2	5.7
	18.7	3.5	5.4
4	16.4	3.6	4.6
	17.4	3.7	4.6
2	16.5	5.7	2.9
	17.0	7.1	2.4
1	14.1	7.4	1.9
	13.6	7.2	1.9

If we assume that the products at the start of the reaction are the same as those at quarter-time, we can calculate from the data of Table II how much of the pressure increase is to be apportioned to the ethylene oxide decomposition and how much to that of butane. Actually this assumption is open to some objection, but it cannot be very far wrong. We thus get the data of Table IV.

TABLE IV

CHAIN LENGTHS IN ETHYLENE-OXIDE–BUTANE MIXTURES

Approximate ratio $\frac{\text{butane}}{(CH_2)_2O}$	Initial rate, mm. per min.	Ethylene oxide decomposition, mm. per min.	Butane decomposition, mm. per min.	Chain length
0 : 1	5.0	5.0	0.0	—
1 : 1	6.6	2.3	4.3	2.9
2 : 1	9.7	2.7	7.0	4.9
4 : 1	15.0	2.7	12.3	8.3
8 : 1	20.4	3.1	17.3	11.5

It will be seen that the apportionment of the rate of pressure increase on the basis of the analyses leads to the conclusion that the initial rate of decomposition of ethylene oxide in the presence of butane is only about one-half the normal rate. No great significance is to be attached to the drift of the last four figures in Column 3 of Table IV, since the assumption that the initial products are the same as those at quarter-time is only approximate.

In the calculation of the chain length from the data of Columns 3 and 4 of Table IV, consideration must be given to the mechanism of the ethylene oxide decomposition. According to Fletcher and Rollefson (9), in the ordinary decomposition of ethylene oxide 0.3 methyl radicals are formed per molecule of ethylene oxide decomposed. This conclusion is based, in the first place, on Sickman's discussion (24) of the mechanism of the ethylene oxide decomposition. He concluded that the complexities in the reaction could be explained on the assumption that the mechanism is

$$\begin{array}{lrcl}
(1) & (CH_2)_2O & = & 2R \\
(2) & (CH_2)_2O & = & CH_3CHO \\
(3) & R + CH_3CHO & = & RH + CH_3CO = RH + CO + R \\
(4) & 2R + M & = & X + M,
\end{array}$$

where R represents a free radical, and M is any third body. All the experimental facts are readily interpreted on this basis if we assume that k_1 is much less than k_2, *i.e.*, that most ethylene oxide molecules isomerize to acetaldehyde, which then undergoes a radical-sensitized decomposition, and that relatively few ethylene oxide molecules give free radicals by Reaction (1). It should be noted that the sensitized decomposition of the acetaldehyde will not affect the radical concentration, since each radical removed by Reaction (3) is regenerated.

It follows that if ethylene oxide is used as a sensitizer in the butane decomposition, the chain length will not be given by

$$\frac{\text{molecules of butane decomposed}}{\text{molecules of ethylene oxide decomposed}},$$

but by

$$\frac{\text{molecules of butane decomposed}}{(\text{molecules of ethylene oxide decomposed}) \,.\, F},$$

where F is the number of free radicals produced per molecule of ethylene oxide decomposed. The Sickman mechanism, by requiring k_1 to be much less than k_2, necessitates that F should be much less than 1, and hence that the chain length shall be greater than a direct calculation from the butane–ethylene-oxide ratio would indicate.

Fletcher and Rollefson investigated the ethylene oxide decomposition with special emphasis on the role of free radicals. Their work led them to postulate a mechanism of the type suggested by Sickman, but of a more detailed nature:

$$\begin{array}{lrcl}
(1) & (CH_2)_2O & = & HCHO + CH_2 \\
(2) & (CH_2)_2O & = & CH_3CHO \\
(3) & CH_2 + (CH_2)_2O & = & 2CH_3 + CO \\
(4) & CH_3 + CH_3CHO & = & CH_3 + CH_4 + CO \\
(5) & 2CH_3 & = & C_2H_6 .
\end{array}$$

This mechanism is in good agreement with their rate measurements, analyses for acetaldehyde and formaldehyde, etc. By assuming that all the hydrogen found in the products comes from the decomposition of formaldehyde formed by Reaction (1), and that all the ethane comes from Reaction (5), they calculate that 14% of the ethylene oxide decomposes by Reaction (1). Whence, since each methylene gives rise to two methyls, they conclude that 0.3 methyls are formed for each ethylene oxide molecule decomposed.

While it cannot be said that this mechanism is established, it is undoubtedly plausible, and all the evidence indicates that by no means all the ethylene oxide decomposes by way of free radicals. It seems very unlikely that Fletcher and Rollefson's estimate of the fraction of ethylene oxide molecules giving rise to radicals is too low, although it may well be too high, since hydrogen and ethane may arise in other ways.

Now, the effect of butane in diminishing the rate of the over-all pressure increase, or the over-all production of carbon monoxide, must obviously be due to the suppression of Reaction (4), since butane can compete with acetaldehyde for methyl radicals produced by Reaction (3). Obviously, however, the presence of butane can have no appreciable influence on the primary steps, Reactions (1) and (2). It follows therefore that in the presence of butane the total number of radicals produced per unit time will remain constant, although the total number of molecules of carbon monoxide produced will diminish, as will the total pressure increase. Hence if the pressure increase due to the ethylene oxide decomposition falls in the presence of butane from 5.0 mm. per min. to, say, 3.1 mm. per min., we may assume that the number of radicals produced per carbon monoxide molecule formed rises from 0.3 to $\frac{0.3 \times 5.0}{3.1} = 0.485$. On this basis we obtain the chain lengths given in Column 5 of Table IV. It may be emphasized that these are minimum chain lengths, and that if fewer free radicals are produced than is indicated by the conclusions of Fletcher and Rollefson, the real chain lengths will be greater than those given.

It was pointed out above that it is very unlikely that *more* free radicals are produced from ethylene oxide than Fletcher and Rollefson suggest. Support for this conclusion is obtained from the work of Frey (10), who investigated the butane decomposition sensitized by methyl radicals from the decomposition of dimethyl mercury. On the assumption that two methyl radicals are formed for each molecule of mercury dimethyl decomposed, he estimated a chain length of about 20. Since there is little doubt that methyl radicals are also the chain carriers in the ethylene oxide sensitized decomposition, it is unlikely that the chain length should be very different from that obtained in Frey's work. Furthermore, the work of Cunningham and Taylor (1) on the decomposition of mercury dimethyl indicates the possibility that only a portion of the mercury dimethyl molecules give radicals. There is thus the possibility that the real chain length in Frey's work was considerably greater than 20. It therefore appears very unlikely that the chain length in the ethylene oxide sensitized decomposition should be less than 10, and it is quite probable that it is greater than this value.

(C) Ethylene-oxide–Nitric-oxide Mixtures

Before proceeding to a study of the three component mixtures it was obviously necessary to investigate the effect of nitric oxide on the rate of decomposition of ethylene oxide. Otherwise it would not be possible to tell whether a diminution in the rate of the sensitized butane decomposition were to be ascribed to a suppression of chain processes in butane, or to an inhibition of the decomposition of the sensitizer. A series of experiments was therefore made with a constant initial pressure of ethylene oxide (7 cm.), and varying amounts of nitric oxide. The complete data of these experiments are plotted in Fig. 3, and the initial rates are given in Table V.

The inhibiting effect of nitric oxide on the ethylene oxide decomposition is evidently considerable, and due allowance must be made for this in considering the three component mixtures.

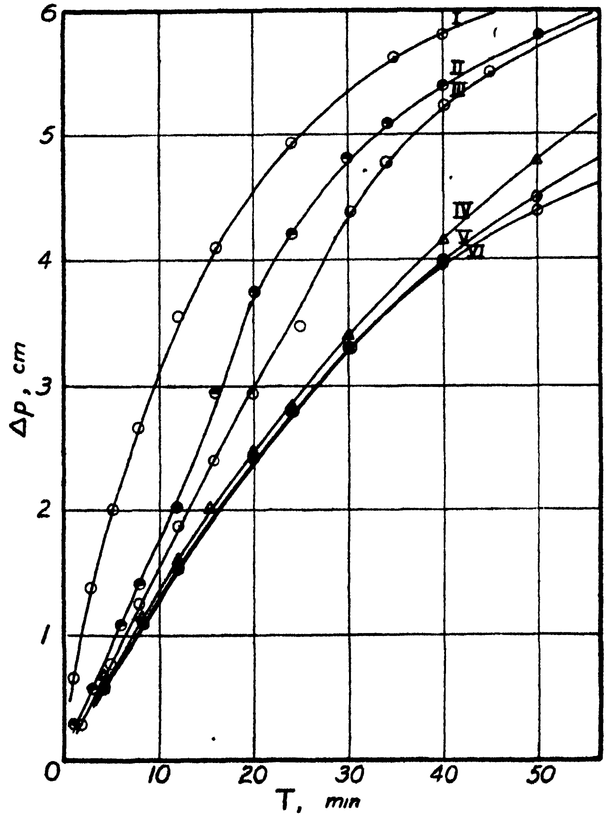

FIG. 3. *Ethylene-oxide–nitric-oxide runs at 450° C. Ethylene oxide at a constant initial pressure (approx. 7 cm.).*

Curve	*I*	*II*	*III*	*IV*	*V*	*VI*
Approx. ratio ethylene oxide/NO	*1 : 0*	*16 : 1*	*8 : 1*	*4 : 1*	*2 : 1*	*1 : 2*

These results are somewhat contrary to the findings of Fletcher and Rollefson who reported that the addition of small quantities of nitric oxide to ethylene oxide increased the induction period but did not change the rate of pressure increase thereafter. In our experiments the induction period was of much smaller duration, and there is no question that the maximum rate of pressure increase was decreased by the addition of nitric oxide. However, our experiments were carried out at a somewhat higher temperature, and the lowest nitric oxide concentration employed by us was about twice the highest concentration employed by them. There seems to be no doubt in any case that, in agreement with the conclusions of Fletcher and Rollefson, the action of nitric oxide is to inhibit the induced decomposition of acetaldehyde, and not the primary process. This is not in accord with the findings of Verhoek (35).

TABLE V

ETHYLENE-OXIDE–NITRIC-OXIDE MIXTURES

Approximate ratio $\frac{\text{ethylene oxide}}{\text{NO}}$	Ethylene oxide pressure, cm.	Nitric oxide pressure, cm.	Initial rate, mm. per min.
1 : 0	7.15	0.00	5.04
16 : 1	7.11	0.41	1.81
8 : 1	7.20	0.95	1.60
4 : 1	7 04	1 80	1.38
2 : 1	7.25	3 65	1.38
1 : 2	6.77	14 67	1.56

Analyses were also made at quarter-time on runs with a 4 : 1 ethylene-oxide–nitric-oxide mixture, and with pure ethylene oxide. These gave values for the ratio

$$\frac{\text{unsaturated hydrocarbons}}{\text{CO}}$$

of 0.012 for pure ethylene oxide, and of 0.015 for the mixture. It is therefore evident that the amount of unsaturates formed from ethylene oxide, both alone and in the presence of nitric oxide, is so small that no appreciable error is introduced when the unsaturates/CO ratio is used as an indication of the relative amounts of butane and of ethylene oxide decomposed. Furthermore, these analyses indicated that at quarter-time a large amount of nitric oxide is still left in the system, in spite of the fact that the inhibition has almost ceased at this stage.

(D) Butane–Ethylene-oxide–Nitric-oxide Mixtures

In these experiments the partial pressure of ethylene oxide was maintained approximately constant at 7 cm. to enable a comparison with the results of the previous section. The butane pressure was maintained constant at 28 cm., and the partial pressure of nitric oxide was varied over a wide range. The complete data are plotted in Fig. 4, and the initial rates of pressure increase are given in Table VI.

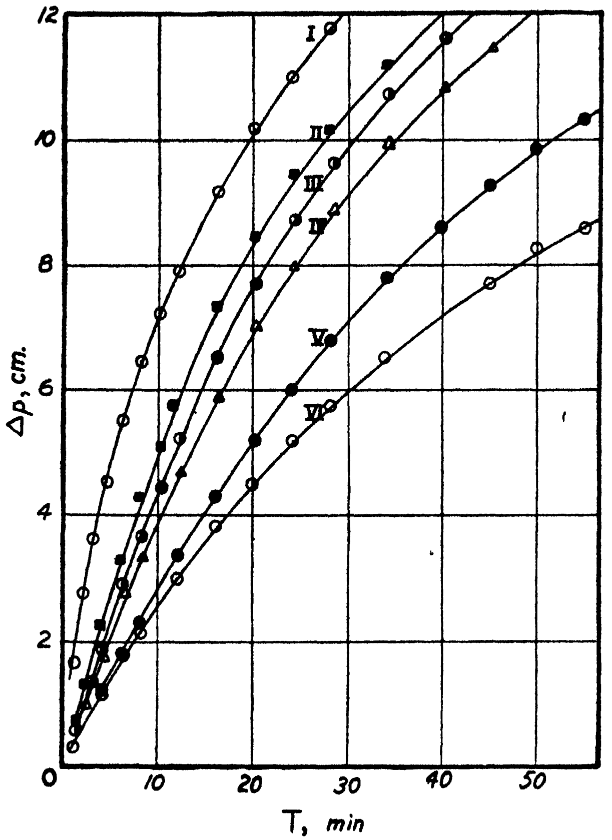

FIG. 4. *Butane–ethylene-oxide–nitric-oxide runs at 450° C. Butane and ethylene oxide at constant initial pressures (approx. 28 cm. and 7 cm. respectively).*

Curve	*I*	*II*	*III*	*IV*	*V*	*VI*
Approx. ratio ethylene oxide/NO	*1 : 0*	*16 : 1*	*8 : 1*	*4 : 1*	*2 : 1*	*1 : 1*

If it is assumed that the ethylene oxide decomposition will proceed at the same rate in the three component mixture as in an ethylene-oxide–nitric-oxide mixture, chain lengths can be calculated from the data of Table VI. The calculations have been made in a manner similar to that used in Section (B), *i.e.*, it is assumed that the inhibiting effect of nitric oxide on the ethylene oxide decomposition results in a lower rate of pressure increase, but does not alter the rate of the primary production of free radicals. We thus arrive at the values given in Column 8. In these calculations we have neglected the inhibiting effect of butane on the ethylene oxide decomposition since this

TABLE VI

BUTANE–ETHYLENE–OXIDE–NITRIC-OXIDE MIXTURES

Butane, cm.	Ethylene oxide, cm.	Nitric oxide, cm.	Approximate ratio $\frac{(CH_2)_2O}{NO}$	Initial rate of pressure increase, mm. per min.	Initial rate in ethylene-oxide-nitric-oxide mixtures	Moles of butane decomposed per mole of ethylene oxide decomposed	Chain length
28.09	6.96	0.00	1 : 0	15.3	(5.04)	—	8.3
27.95	6.96	0.44	16 : 1	6.30	1.81	2.5	3.0
28.30	6.98	0.84	8 : 1	5.17	1.60	2.3	2.5
28.77	7.09	1.78	4 : 1	4.70	1.38	2.4	2.2
28.42	7.18	3.53	2 : 1	3.25	1.38	2.0	1.8
27.86	7.04	7.08	1 : 1	3.04	1.56	1.0	1.0

effect will be small compared to that of nitric oxide. As a result of this approximation the calculated chain lengths may be slightly low. To decide the question analyses were made at quarter-time of the products from the three component mixtures. The results of these are given in Table VII.

All things considered, the agreement of the mean chain lengths with those given in Table VI is quite satisfactory. The values given in Table VII are probably the more reliable. It thus appears that the addition of nitric oxide cuts down the chain length in the ethylene oxide sensitized butane decomposition from about 10 to 1.5, but that no matter how high the nitric oxide concentration may be the chain length cannot be reduced much below this value.

TABLE VII

BUTANE–ETHYLENE-OXIDE–NITRIC-OXIDE MIXTURES. ANALYSES AT T_{25}

Approximate ratio $\frac{(CH_2)_2O}{NO}$	Products, mole per cent			$\frac{C_nH_{2n}}{CO}$	Chain length
	NO	C_nH_{2n}	CO		
1 : 0	—	16.4	3.6	4.6	8.3
	—	17.4	3.7	4.6	8.3
16 : 1	0.31	14.9	5.0	3.0	3.6
	0.52	15.4	6.1	2.5	3.0
4 : 1	1.1	13.2	7.5	1.8	1.65
	0.8	13.9	6.6	2.1	1.9
2 : 1	1.6	12.7	7.9	1.6	1.45
	2.1	12.8	8.9	1.4	1.3
1 : 1	6.4	12.4	8.5	1.5	1.55
	6.3	12.5	8.9	1.4	1.45
1 : 2	14.5	10.4	7.0	1.5	1.55

Discussion

The use of nitric oxide as an indicator for the presence of chains in organic decompositions involves the assumption that maximum inhibition corresponds to the complete suppression of chains. The present results show that this assumption is not entirely justified, since in the ethylene oxide sensitized decomposition of butane maximum inhibition corresponds to a chain length of 1.5 or greater. It is therefore almost certain that maximum inhibition does not correspond to the complete suppression of chains in the normal decomposition of butane, and perhaps also in many other cases. The chain lengths calculated from nitric oxide inhibition must therefore be regarded as minimum chain lengths, and it is possible in any individual case, and particularly so with the hydrocarbons, that the real chain lengths are greater than the nitric oxide method would indicate, and they may be very much greater. On the assumption of Fletcher and Rollefson that 0.3 radicals are formed per ethylene oxide molecule decomposed, the minimum chain length found here is 1.5, which would correspond to 4.0 in the normal decomposition of butane if we assume that two radicals are formed in the primary step. It has been pointed out above, however, that it is quite probable that less radicals are formed in the ethylene oxide decomposition than Fletcher and Rollefson conclude. If this is the case, then the chain length at maximum inhibition in the present investigation is much higher than 1.5, and this may also be true for many other reactions.

As pointed out in the Introduction, there has been considerable discussion as to whether the chain lengths obtained by the nitric oxide inhibition method are to be interpreted as actual chain lengths, or whether they are merely mean values and actually there are very few chains but these are long. It has been suggested in some cases that the real chain lengths are as high as 10^5 to 10^7. It is obvious that in the sensitized decomposition of a substance we have a more or less definite idea of the number of primary acts on the part of the sensitizer, and hence the chain length under these circumstances is the average length of the chains which are really started. Now the chains in the ordinary decomposition of butane are undoubtedly carried by radicals which are the same as, or similar to, those which are effective in the sensitized decomposition. There seems therefore to be no justification for the assumption that the actual chain lengths in the two cases are of quite different orders of magnitude. In our opinion, therefore, there is no justification for the conclusion that there are merely a few very long chains in the normal decomposition of butane. It is perhaps worth pointing out that the assumption of a few very long chains in the ethylene oxide sensitized reaction would lead to difficulties. Thus suppose that we assume a few chains with a length of, say, 10^6 units. Then, since nitric oxide only reduces the mean chain length by a factor of 5 to 10, it would be necessary to assume a chain length of about 10^5 under circumstances corresponding to maximum inhibition by nitric oxide.

It seems to be generally accepted that the mechanism of nitric oxide inhibition is the formation of an addition compound between a radical and nitric oxide. Various detailed schemes have been proposed in specific cases. The following generalized scheme, proposed by Rice and Polly (20), is in agreement in principle with the suggestions of other workers:

(1) $M_1 = 2\,R_1$
(2) $M_1 + NO = HNO + R_2$
(3) $R_1 + M_1 = R_1H + R_2$
(4) $R_2 = R_1 + M_2$
(5) $R_1 + NO = R_1NO$
(6) $2\,R_1 = R_1R_1$
(7) $R_2 + NO = R_2NO$
(8) $R_1 + R_2 = R_1R_2$

Rice and Polly then suggest two different schemes:

I. Reaction (4) has a low activation energy. The chains therefore end by Reactions (5) and (6).

II. Reaction (4) has a high activation energy, and the chains end by Reactions (7) and (8).

If we accept Scheme II, and assume that Reaction (3) is fast, then chains will be stopped only by combination of R_2 and NO, and not by combination of R_1 and NO. Under these circumstances nitric oxide would be unable to break chains until one link later than the primary step. In the present case, therefore, if it is assumed that maximum inhibition corresponds to a chain length of about 1.5 the result could perhaps be explained on this mechanism, and at maximum inhibition all chains would be suppressed after the second link. However, for the reasons outlined above, it is possible that the chain lengths are much greater than Fletcher and Rollefson's mechanism indicates, and hence that the chain length at maximum inhibition is considerably greater than 1.5. If this is the case it appears that either

(a) Some reaction like (2) is promoting chain decomposition and competing with Reactions (5) or (7) which break chains. Maximum inhibition is therefore a balance between the two opposing factors and does not correspond to the complete suppression of chain processes.

Or

(b) There are two distinct types of chain process, only one of which is susceptible to inhibition by nitric oxide.

In any case the present results cast some suspicion upon the idea that maximum inhibition by nitric oxide in all cases corresponds to complete suppression of chains. The possibility must therefore not be overlooked that free radical chain processes may exist which are not indicated by the action of nitric oxide.

One further point merits discussion. We have found, as did Echols and Pease, that the initial inhibition by nitric oxide falls off with time. Now the decrease in the first order constants in the butane and other hydrocarbon decompositions as a run progresses suggests, as Dintzes and Frost have pointed out (2, 3, 4), that the products of the reaction have an inhibiting effect. Rice and Polly have recently investigated the inhibiting effect of propylene on a number of reactions and have found that it is quite efficient in suppressing free radical chain processes. It therefore seems likely that as the butane decomposition progresses and the concentration of olefines increases, the inhibiting effect of the olefines will swamp out that of the added nitric oxide, and as a result the rate of the nitric oxide inhibited reaction will approach the normal rate in the later stages of the reaction.

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A STUDY OF THE MECHANISM AND KINETICS OF THE SULPHITE PROCESS[1]

BY J. M. CALHOUN[2], F. H. YORSTON[3], AND O. MAASS[4]

Abstract

The rate of delignification of resin extracted spruce wood-meal has been determined in calcium-base sulphite liquor at temperatures from 130° C. down to 50° C. No break was found in the temperature coefficient curve at the lower temperatures, the reaction following the Arrhenius equation closely. Possible mechanisms of the reaction are discussed in the light of existing theories, and the effect of temperature on the yield of pulp is pointed out for its practical interest.

Introduction

A study of the kinetics of a chemical reaction is usually made by measuring the reaction velocity at different temperatures and at different initial concentrations of each reactant over as wide a range as possible. In the case of the delignification of wood in sulphite liquor, the problem is complicated by the large number of variable factors involved and by the heterogeneous nature of the reaction. Nevertheless, it was felt that an investigation of the effect of liquor composition and temperature on the rate of delignification would throw some light on the mechanism and kinetics of the reaction.

The variation in the rate of delignification of spruce wood with the liquor composition has previously been determined and reported by the authors, both for calcium-base (1) and magnesium-base liquor (2). With regard to the variation in reaction rate with temperature, very little quantitative information is available. Stangeland (11) made some small-scale laboratory cooks and reported that the rate of removal of "incrustants" (all materials other than Cross and Bevan cellulose) was approximately first order, and that the temperature coefficient was close to 2.0 per 10° interval between 110° and 140° C. Yorston (12, 13) found that the rate of removal of lignin showed a systematic deviation from the first order relation. Corey and Maass (3) cooked two samples of wood-meal at several temperatures, and assuming a first order relation showed that the variation in reaction rate with temperature followed the Arrhenius equation between 100° and 140° C.

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Contribution from the Department of Physical Chemistry, McGill University, Montreal, Canada. This investigation was carried out in co-operation with the Forest Products Laboratories of Canada, Montreal, and formed part of the research program of that institution.

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It was desired to repeat the latter work more accurately and over a greater temperature range. Particular interest lay, for several reasons, in low temperature cooks. It has been a common belief in the sulphite industry that wood cannot be satisfactorily delignified below 110° C., and Sankey and Hibbert (10) have stated that the sulphonation reaction does not take place below this temperature. If this were true, a change in the slope of the temperature coefficient curve would be expected; this might give a clue to the mechanism of the reaction. A quantitative study of the effect of temperature on the yield of pulp is of both theoretical and practical interest.

Experimental

The experimental procedure followed was identical in every detail with that previously described for the determination of the effect of liquor composition (1). Well seasoned, white spruce wood-meal (density, 0.43; mesh, 40 to 100) was prepared from the same log and extracted with alcohol benzene (1 : 2). The lignin content was 27.5%. All cooks were carried out in 100 cc. sealed Pyrex bomb tubes with calcium-base sulphite liquor containing initially about 1.0% combined, and 10% free, sulphur dioxide. The liquor ratio (50 : 1) was sufficiently large to minimize any concentration changes during cooking. Six samples of wood-meal were cooked for different lengths of time at each temperature in an oil bath thermostatically controlled to within 0 1° C.

The mean liquor concentration for a given run was taken as the average of that for all the bombs, analysis being made after cooking. The liquor concentration as determined at room temperature was corrected, in the manner previously described, for the sulphur dioxide lost to the vapour phase at cooking temperatures. The observed time of cooking was that recorded from the moment the bombs were dropped into the bath until they were quenched in water. A correction for the time required to heat the bombs to the cooking temperature, in terms of the time required to do the same amount of cooking at that temperature, was determined and applied as described before. This amounted to −0.22 hr. at 130° C., −0.18 hr. at 110° C., and was insignificant at lower temperatures. The cooked wood-meal was filtered, washed, oven dried, weighed, and analyzed for lignin by the Ross-Potter method (9). All yields were calculated on the resin extracted, bone-dry wood basis.

Results

The Effect of Temperature on the Yield of Pulp

Cooks were made at 50°, 70°, 90°, 110°, and 130° C.; the results are given in Table I. Since pulp yields must be compared on the basis of the same lignin content, the effect of temperature on yield can be most clearly shown by plotting the yield of pulp against the percentage lignin removed in each cook. This has been done in Fig. 1, and it is observed that the yield of pulp at any given lignin content decreases with increase in the cooking temperature. The yields of pulp at 50, 80, 90 and 95% delignification were determined from

TABLE I

THE EFFECT OF TEMPERATURE ON THE RATE OF DELIGNIFICATION OF SPRUCE WOOD AND YIELD OF PULP

I	II	III	IV	V	VI	VII	VIII
Time in bath (uncorrected), hr.	Combined sulphur dioxide, %	Total sulphur dioxide (uncorrected), %	Total sulphur dioxide (corrected) %	Yield of pulp, %	Yield of non-lignin, %	Lignin, per cent of pulp	Lignin, per cent of original wood
Temperature, 50° C.							
150	0.95	10.40	10.40	91.6	74.4	18.8	17.2
310	0.95	10.20	10.20	87.8	75.7	13.8	12.1
500	0.95	10.50	10.50	85.6	77.1	9.91	8.48
910	0.98	10.50	10.50	78.7	76.3	2.98	2.35
1510	0.92	10.30	10.30	73.5	72.6	1.23	0.90
Average	0.96	10.38	10.38				
Temperature, 70° C.							
36	0.97	11.08	11.08	87.1	71.1	18.4	16.0
72	0.94	10.96	10.96	81.6	71.7	12.2	9.91
96	0.94	10.96	10.96	78.8	72.3	8.14	6.46
120	0.92	10.78	10.78	75.3	70.5	6.31	4.75
144	0.92	10.72	10.72	72.3	69.6	3.76	2.72
180	0.90	10.58	10.58	69.3	67.8	2.10	1.45
216	0.94	10.82	10.82	66.8	65.9	1.34	0.90
Average	0.93	10.84	10.84				
Temperature, 90° C.							
12.0	0.98	10.88	10.87	79.3	69.1	12.9	10.2
24.0	0.95	10.84	10.82	69.0	66.0	4.39	3.03
36.0	0.94	10.88	10.85	62.2	61.0	1.97	1.23
48.2	0.95	10.68	10.66	59.3	58.5	1.26	0.75
Average	0.95	10.82	10.80				
Temperature, 110° C.							
2.00	0.94	10.60	10.55	78.7	62.8	20.2	15.9
4.00	0.94	10.60	10.53	69.7	59.9	14.0	9.77
5.50	0.90	10.72	10.62	64.6	59.5	7.97	5.14
8.00	0.90	10.88	10.80	57.5	55.8	2.97	1.71
10.00	0.90	10.92	10.82	54.4	53.6	1.47	0.80
Average	0.91	10.74	10.66				
Temperature, 130° C.							
0.50	0.96	11.06	10.90	81.0	61.4	54.2	19.6
1.00	0.92	11.06	10.92	69.6	57.2	17.8	12.4
1.50	0.90	10.88	10.75	62.0	55.2	10.96	6.80
2.00	0.83	10.72	10.59	55.7	52.9	4.96	2.76
2.50	0.84	10.80	10.61	52.1	50.8	2.55	1.33
3.00	0.78	10.36	10.15	50.4	49.4	1.93	0.97
Average	0.87	10.81	10.65				

these curves and replotted against the temperature in Fig. 2. The horizontal dotted lines represent the maximum yields possible, *i.e.*, the sum of the lignin plus the original non-lignin content of the wood. The actual yields approach their maximum values below 70° C. That is, very little or no carbohydrate material is removed from the wood at these lower temperatures.

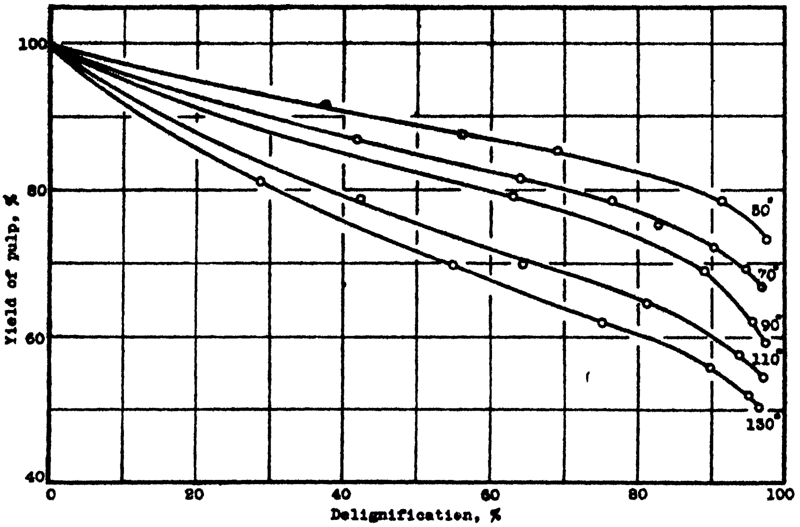

FIG. 1. *The effect of temperature on the yield of pulp.*

It should be mentioned that the yields of non-lignin reported at 50°C. in Table I appear to be anomalous, as they are slightly higher than the non-lignin content of the original wood (72.5%). The only explanation would seem to be that the lignin values are in error, because the non-lignin is obtained by difference. However, the lignin analysis was done in duplicate for this particular run and good checks were obtained.*

The curves in Fig. 2 show a slight tendency to flatten out at the higher temperatures. This is to be expected since some of the carbohydrate material is much more resistant than the remainder. Nevertheless it is clear that temperatures of 150° C., which are sometimes reached in commercial pulping, would be extremely harmful from the point of view of yield. The practical advantage of very low cooking temperatures in increased yields of pulp is offset by the long time required for cooking. However, an intermediate cooking temperature of, say, 90° C., using a liquor high in free sulphur dioxide, might result in an improvement in quality as well as a high yield.

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* *Since the above was written, J. Cannon, in this laboratory, has determined holocellulose, chlorine number, and lignin by the 72% sulphuric acid method in pulps cooked at 70°, 100°, and 130° C. The delignification at the lowest temperature, as judged by these analyses, is less than that indicated by the Ross-Potter method. Temperature coefficients of the pulping reaction based on chlorine number or on residual lignin as determined by 72% sulphuric acid appear to be about 5% greater than the coefficient calculated from analyses by the Ross-Potter method. The discrepancy seems to be due to a peculiarity of the sulphonated lignin in pulp cooked at a very low temperature; such lignin is slightly soluble under the conditions of the Ross-Potter analysis.*

The Temperature Coefficient of Delignification

The lignin remaining in the pulp after each cook, calculated as a percentage of the original wood, is plotted on a logarithmic scale against the observed time of cooking in Fig. 3. These delignification curves are all similar in shape and show the same deviation from the straight line, first order relation reported by Yorston (12) and others (1, 2, 3). The curve obtained at 50° C. proves that wood can be delignified by the sulphite process at this temperature, a fact that is contrary to general belief. This statement is true, regardless of possible small errors in lignin analysis for this run, which would only slightly alter the shape of the curve. However, a reservation must be made regarding the validity of the velocity constants calculated for this run until further investigation has been made.

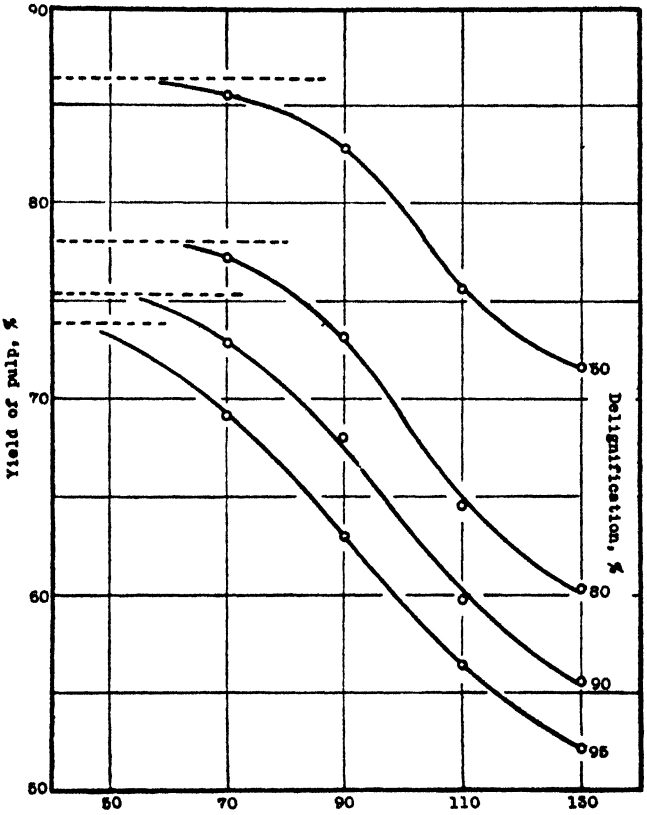

FIG. 2. *The effect of temperature on the yield of pulp.*

The calculation of the temperature coefficient of delignification is complicated by the deviation of the reaction from the first order relation, since an estimation of velocity constants is necessary. However, the following method was adopted. The observed times required to bring about 50, 80, 90, and 95% delignification at each temperature were read from the curves in Fig. 3; these are listed in Table II. The time correction was then applied for the cooks made at 110° and 130° C. by subtracting 0.18 and 0.22 hr. respectively. Finally, all the times were corrected to correspond to cooking with the same concentration of free sulphur dioxide (9.75%). This was necessary because it was impossible to predetermine the exact liquor composition, and small variations resulted from run to run. This correction was readily made since the authors have shown (1) that the time of cooking at constant combined, is inversely proportional to the concentration of free, sulphur dioxide, at least over short ranges.

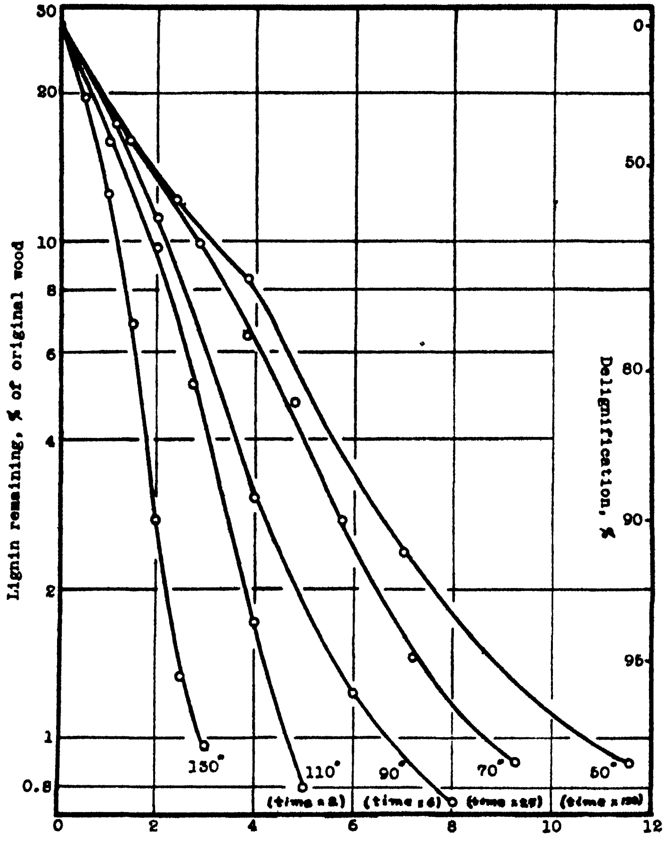

FIG. 3. *The effect of temperature on the rate of delignification.*

First order velocity constants were then calculated for the ranges 0 to 50%, 50 to 80%, 80 to 90%, 90 to 95% delignification, all expressed in units of seconds. Although these velocity constants vary at different stages in the cooking process at any one temperature as expected, it is believed that the mean velocity constants calculated in this manner represent as fair a value as it is possible to obtain.

TABLE II

CALCULATION OF VELOCITY CONSTANTS AND THE TEMPERATURE COEFFICIENT OF DELIGNIFICATION

Temperature, °C.	50	70	90	110	130
Average concentration of sulphur dioxide, % (corrected)					
Total	10.38	10.85	10.80	10.66	10.65
Combined	0.96	0.93	0.95	0.91	0.87
Free	9.42	9.92	9.85	9.75	9.78
Time, hr. (observed)					
To 50% delignification	245	48	8.80	2.59	0.90
To 80% delignification	655	109	18.4	5.36	1.64
To 90% delignification	855	143	25.1	6.80	2.00
To 95% delignification	1180	184	33.8	8.45	2.47
Time, hr. (corrected for time required to reach temperature)					
To 50% delignification	245	48	8.80	2.41	0.68
To 80% delignification	655	109	18.4	5.18	1.42
To 90% delignification	855	143	25.1	6.62	1.78
To 95% delignification	1180	184	33.8	8.27	2.25
Time, hr. (corrected to 9.75% free sulphur dioxide)					
To 50% delignification	237	48.8	8.88	2.41	0.68
To 80% delignification	632	111	18.6	5.18	1.42
To 90% delignification	826	145	25.3	6.62	1.78
To 95% delignification	1140	187	34.1	8.27	2.25
First order velocity constants, $k \times 10^5$ (sec.$^{-1}$)					
0–50% delignification	0.0813	0.395	2.17	7.99	28.3
50–80% delignification	0.0644	0.410	2.62	9.19	34.4
80–90% delignification	0.0997	0.567	2.87	13.37	53.5
90–95% delignification	0.0613	0.459	2.19	11.67	41.0
Average	0.0767	0.458	2.46	10.56	39.3
Temperature coefficient per 10° C.		2.44	2.32	2.07	1.93

The approximate temperature coefficient per 10 degrees was calculated for each interval according to the formula

$$\left(\frac{k_2}{k_1}\right)^{\frac{t_2-t_1}{10}}, \tag{1}$$

where k_2 = the velocity constant at the higher temperature, t_2° C.,
k_1 = the velocity constant at the lower temperature, t_1° C.

The calculated values shown at the bottom of Table II are close to 2, which is in agreement with results given in previous reports (3, 11).

If the integrated form of the Arrhenius equation

$$\ln k = \ln Z - E/RT, \tag{2}$$

where k = the velocity constant,
T = the absolute temperature,
R = the molar gas constant,
Z, E = specific constants for each reaction,

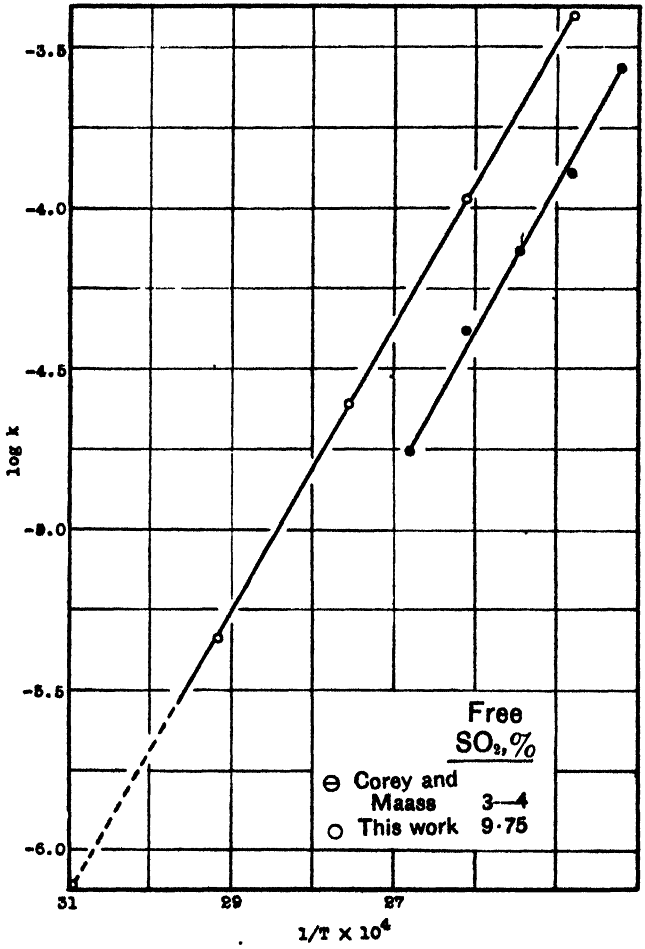

FIG. 4. *The temperature coefficient of delignification.*

is used, an excellent straight line is obtained by plotting the logarithm of velocity against $1/T$, as seen in Fig. 4. The data of Corey and Maass (3), converted from hours^{-1} to seconds^{-1} for comparison, are also plotted in Fig. 4. The magnitudes of the velocities in the two cases differ because different liquor concentrations were used, but the slopes of the two lines (and hence the values of E) are almost identical.

The constants of the Arrhenius equation for the delignification of wood were calculated for our data from the straight line in Fig. 4 and found to be:

$$E = 20{,}200 \text{ cal. per gm. mole}$$

$$Z = 3.42 \times 10^7 \text{ sec.}^{-1}$$

The variation in the rate of delignification with temperature for the sulphite process under the experimental conditions chosen is therefore expressed by the equations:

$$\ln k = 17.3 - 20{,}200/RT \qquad (3)$$

or

$$k = 3.42 \times 10^7 \, e^{-20{,}200/RT} . \qquad (4)$$

The value of E reported by Corey and Maass is 21,000 cal. per gm. mole, which is good agreement when the errors involved are considered. The constant Z, of course, depends on the concentration of the cooking liquor.

The fact that the delignification of wood in sulphite liquor obeys the Arrhenius equation over the temperature range investigated shows that there is no critical temperature, such as 110° C., below which the reaction does not proceed normally. The temperature appears to affect only the velocity of delignification as in the case of comparatively simple chemical reactions. This is true even if we consider the velocity constant calculated at 50° C. unreliable for the reasons already stated. The cooks made at 70° and 90° C. provide sufficient evidence that the reaction obeys the Arrhenius equation below 110° C.

Discussion

The Temperature Coefficient of Delignification

The fact that the delignification reaction obeys the Arrhenius equation rigidly over a considerable temperature range, and in spite of all the complex factors involved, suggests the possibility of a conventional interpretation based on the activation theory of molecular collisions. The authors have shown previously (1) that the active cooking agent in calcium-base sulphite liquor appears to be free sulphurous acid or the hydrogen and bisulphite ions together, and that cooking action cannot be attributed to either ion alone. Let us suppose then, that delignification consists essentially of a reaction between lignin and sulphurous acid. Yorston (14) has provided considerable evidence that all parts of the lignin are accessible to the reagent, and the diffusion rates (in the case of wood-meal) appear to be high enough that we may neglect, for the moment, the heterogeneous nature of the reaction.

In the case of the delignification of wood, we do not know what the lignin "molecule" is. Nevertheless, lignin may be pictured as existing in a number of repeating units or aggregates of unknown size, which in the presence of a peptizing medium may undergo slight molecular motion within the confines allowed by the structure as a whole. The combination of a lignin unit with one or more molecules of sulphurous acid yields a lignin sulphonic acid which is subsequently dissolved or peptized away. The fact that the reaction involves two molecular species, but is not second order, may be explained by the large excess of sulphurous acid. That is, the reaction is merely pseudo-unimolecular. This would indicate a linear relation between the rate of delignification and the concentration of free sulphur dioxide which is approximately borne out by experiment (1).

Moelwyn-Hughes (8) has derived a theoretical value of Z for all uncomplicated bimolecular reactions in solution which is of the order of 10^{11} sec.$^{-1}$ This is due to the compensating effect of two opposing factors, *viz.*, the larger the molecule, the smaller is its velocity, but the larger is its collision area. Consequently, the theoretical collision frequency is approximately constant, and the theoretical reaction velocity will be determined by the energy required for activation. In the delignification of wood, the experimental value of Z is of the order of 10^7 sec $^{-1}$. In other words, the collision frequency appears to be lower than the theoretical value by a factor of 10^4. Or rather, only one collision in 10,000 having the requisite energy (20,200 cal. per gm. mole) results in reaction. This abnormally low velocity has been observed with a number of relatively simple reactions in solution known to be bimolecular, for which Moelwyn-Hughes offers a number of explanations. The most probable one in the present case is that stringent conditions of orientation are required. In view of the size and complexity of the lignin molecule, it is not unreasonable that a reaction should take place only when an activating collision occurs at a certain point.

The value of the critical energy E found for the sulphite process (20,200 cal. per gm. mole) is of the same order of magnitude as that for homogeneous bimolecular reactions in solution. This value may be compared with 32,000 cal. reported by Larocque (7) for the alkali process.

The Rate of Delignification at a Fixed Liquor Composition

Since there is always a large excess of sulphurous acid present during the delignification reaction, we would expect the instantaneous rate of removal of lignin in any one sulphite liquor to be proportional to the quantity of lignin remaining undissolved (*i.e.*, a first order reaction) provided:

(*a*) That all the lignin is equally accessible to the reagent,
(*b*) That the lignin is chemically homogeneous,
(*c*) That only one chemical reaction takes place, or, if there is a series of consecutive reactions, one reaction is slow enough in comparison with the others to be rate determining.

Experimentally, the delignification reaction closely approximates, but does not actually follow, the monomolecular law. The regular deviations from the first order relation cannot be due to the consumption of sulphur dioxide as the reaction proceeds, since the shape of the delignification curve was found to be the same over a wide range for all the liquor concentrations tried (1). In addition, the analysis of the liquor after cooking showed that only very slight concentration changes occurred during cooking. The deviation is therefore real.

The evidence of Yorston (14) is fairly strong that all the lignin is accessible to the reagent. Hence, the consistent departure of the reaction from the first order relation may be due to the non-fulfilment of conditions *(b)* or *(c)*. Since lignin is a complex biological product, there is reason to believe that it is not chemically homogeneous. Lignin sulphonic acids recovered from waste sulphite liquor can be separated into two distinct fractions, although it has been suggested that the difference is one of molecular aggregation rather than chemical behaviour. In addition, the decrease in rate toward the end of the reaction has frequently been attributed to the existence of a more resistant fraction of lignin.

Yorston (14) has developed the hypothesis of two consecutive monomolecular reactions, and has shown that the shape of the delignification curve can be explained on this basis, provided that the velocity constants of the two reactions do not differ by a factor of more than about 2. It was suggested that the rate of sulphonation might be proportional to the quantity of unsulphonated lignin present at any instant, and that the rate of removal of lignin might be proportional to the quantity of sulphonated lignin present at any instant. However, it was found that the actual rate of removal of lignin could not be predicted in this manner, and it was concluded that more sulphur than that required for delignification was taken up by the lignin.

The actual mechanism by which sulphonated lignin is removed from the wood has still to be explained. The delignification mechanism proposed by Hägglund (4, 5) is based on the assumption of a rapid sulphonation reaction, followed by the hydrolysis of a hypothetical lignin-sulphonic-carbohydrate complex, the rate of which is supposedly governed by the hydrogen ion concentration of the liquor which would determine the over-all rate of cooking. This theory is quite untenable since the authors have shown (1) that the rate of delignification is not controlled by the hydrogen ion concentration alone, even in the final stages of the reaction when the lignin is highly sulphonated.

Kullgren (6) has proposed a slightly different mechanism, suggesting that there is an equilibrium between the free lignin sulphonic acid and its calcium salt, and that only the former is soluble. He maintains that the rate of delignification is determined by the ratio of the hydrogen ion concentration to the calcium ion concentration, *i.e.*, (H)/(Ca). The authors' results show that this theory is equally untenable, since the rate of delignification was found to be governed by the product of the concentrations of the hydrogen and bisulphite ions. When the concentration of base is kept constant, the rate of reaction does increase with increase in the hydrogen ion concentration, as Kullgren states. However, an increase in the concentration of base also increases the rate of delignification, provided that the hydrogen ion concentration is held constant. This is exactly the reverse of what Kullgren's theory would predict, and is due to the fact that he has ignored the important role played by the bisulphite ion.

The authors' results indicate that whether there is a hydrolysis reaction or not, the sulphonation reaction is more probably the important rate-determining reaction. Since solubility depends on molecular size as well as on chemical similarity, there are two ways in which the lignin may be rendered soluble which do not involve a hypothetical hydrolysis reaction. The introduction of sulphonic acid groups may confer hydrophilic properties on lignin, allowing it to be more easily peptized in a medium of suitable ionic concentration. A depolymerization or rupture of bonds between lignin units may also occur. Both of these processes would tend to increase the solubility of lignin. The greater the depolymerization or the greater the degree of sulphonation, the more readily would the lignin be peptized. Neither process alone seems to be sufficient. Whether there could be any interrelation between the sulphonation reaction and a depolymerization process cannot be stated at the present time. These points cannot be cleared up until more is known concerning the structure and chemistry of lignin itself.

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A STUDY OF THE COLORIMETRIC DETERMINATION OF PYRROLE WITH ISATIN AND THE APPLICATION OF THE METHOD TO BIOLOGICAL MATERIALS[1]

By G. H. Guest[2] and W. D. McFarlane[3]

Abstract

Fromm's method for the determination of minute amounts of pyrrole has been modified and applied to the determination of pyrrole produced by the dry distillation of various substances. The pyrrole obtained from gelatin is derived entirely from the proline and hydroxyproline which it contains. Enzymatic, acid, or alkali hydrolyzates of gelatin, gliadin, and glutenin, contain no detectable amount of free pyrrole. Sodium peroxide markedly increases the yield of pyrrole obtained in the dry distillation of gelatin. The addition of copper sulphate catalyzes the oxidation of proline to pyrrole by sodium peroxide.

Introduction

Two colorimetric reactions have been widely employed for the determination of minute amounts of pyrrole, namely, the production of a pink colour with *p*-dimethylaminobenzaldehyde and the formation of pyrrole-blue by condensing pyrrole with isatin in acid solution. The former reaction is lacking in specificity, being given by substituted pyrroles, pyrrolines, pyrrolidines, and indoles. On the other hand, the isatin reaction is highly specific, being given only by pyrroles with an α-position unsubstituted, and not given by reduced pyrroles or indole derivatives.

Fromm (2) has recently developed for the determination of pyrrole a colorimetric method that employs the isatin reaction. The authors have had occasion to use this method and have found it necessary to make several modifications, which are described in this paper. The application of the method to the determination of pyrrole in biological materials requires the separation of the pyrrole from other decomposition products which interfere with the reaction. For this purpose the conditions for the quantitative precipitation of minute amounts of pyrrole by mercuric chloride, and for the complete extraction of pyrrole by ether, have been investigated. The procedure developed has been applied to the determination of the yield of pyrrole obtained by the dry distillation of various proteins and other substances, and also to determine whether free pyrrole occurs in protein hydrolyzates.

Experimental

I. An Improved Micro-colorimetric Method for the Determination of Pyrrole as Pyrrole-blue

To determine the optimum conditions for the development of the blue colour in the pyrrole-isatin reaction, experiments were conducted with a

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solution of freshly distilled pyrrole in 0.5% acetic acid. This solution is stable for at least one month, whereas a solution of pyrrole in 0.5% hydrochloric acid develops a yellow colour, with appreciable loss of pyrrole, within 24 hr. Fromm (2) carried out the procedure by adding 2 ml. of 6 *N* hydrochloric acid to an aliquot of a solution of pyrrole in 0.5% hydrochloric acid and diluting to 10 ml. To this solution was added 1 ml. of a 0.05% solution of isatin in glacial acetic acid and the mixture heated for 10 min. in a boiling water bath. After the solution had been cooled, the intensity of the blue colour was measured with a step-photometer.

The following observations of Fromm's procedure were made with the aid of a single-cell type of photoelectric colorimeter with light filters, as described by Evelyn (1):— *(a)* Increasing the concentration of hydrochloric acid markedly increased the intensity of the blue colour, the maximum being obtained when the reaction was carried out in 5 to 6 *N* hydrochloric acid. With this concentration of hydrochloric acid the maximum intensity of colour was developed on standing for five minutes at room temperatures. By eliminating the heating on the boiling water bath more reproducible results were obtained. *(b)* It was found that 0.2 ml. of an 0.5% solution of isatin in glacial acetic acid gave the most satisfactory results. More of this reagent slightly increased the intensity of the blue colour but gave too high a galvanometer reading in the control determination. *(c)* Dilution of the reaction mixture with 95%

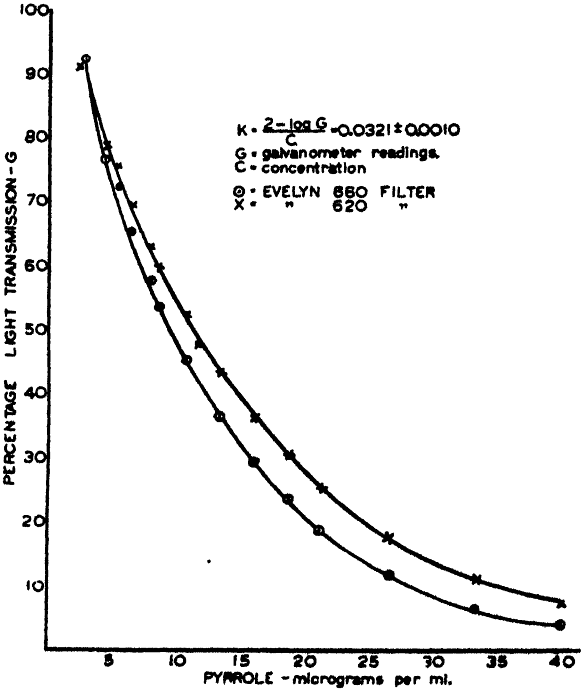

FIG. 1. *Showing the relation between the concentration of pyrrole and the intensity of the pyrrole-blue colour.*

ethyl alcohol instead of water gave a much more intense and more stable blue colour.

The procedure finally adopted was as follows:— 1 ml. of the pyrrole solution, containing 5-30 micrograms of pyrrole per ml., was transferred to a 10 ml. glass-stoppered graduated cylinder and 0.2 ml. of a 0.05% solution of isatin in glacial acetic acid and 1 ml. of concentrated hydrochloric acid were added. After five minutes the mixture was diluted to the 10 ml. mark with 95% ethyl alcohol and the intensity of the blue colour measured with an Evelyn photoelectric colorimeter, using a 660 mu filter. The centre setting of the instrument was determined with a blank solution, prepared in a manner identical with that of the test solution but to which no pyrrole was added. The colour was stable for at least one hour and no significant difference in the colour intensity was observed if the reaction time was varied from 5 to 20 min. The calibration data are shown in Fig. 1 and were obtained by the application of the above procedures to a standard solution of pyrrole. Under these conditions the isatin-pyrrole reaction conforms to Beer's law, the mean value of K being 0.0321 ± 0.0010. The calibration data obtained with the two filters were used to detect any change in the shade of colour particularly when the method was applied to crude materials. The authors have observed that 2,5-dimethylpyrrole, 2-carbethoxypyrrole, 1,2-dicarbethoxypyrrolidine, pyrrolidine, proline, hydroxyproline, tryptophane, and indole failed to react with isatin under the conditions of the test, but 1-carbethoxypyrrole did react.

Fromm (2) has further reported an investigation of the use of mercuric chloride as a precipitant to separate pyrrole from substances which would interfere with the colour reaction. The authors have repeated his experiments and have been unable to confirm the quantitative recovery of pyrrole after precipitating with mercuric chloride, washing the precipitate with alcohol, and finally dissolving the precipitate in 5% sodium cyanide solution. The precipitate is appreciably soluble in 95%, or absolute, ethyl or methyl alcohol; the pyrrole-blue colour is modified by the presence of sodium cyanide, and, further, quantitative precipitation of pyrrole by mercury depends on the pH of the solution, the best results being obtained by buffering the solution with phosphate buffer of pH 6 3.

The procedure which the authors have finally adopted is as follows:— 5 ml. of pyrrole solution, containing 0 158 mg. of pyrrole per ml., were placed in a 15 ml. graduated centrifuge tube and to it was added 5 ml. of a phosphate buffer solution (pH 6.3), and 5 ml. of a saturated aqueous solution of mercuric chloride. The mixture was vigorously stirred and allowed to stand for one hour before centrifuging. The precipitate was washed twice with 10 ml. portions of distilled water. After each washing the supernatant liquid was removed carefully by suction. The precipitate was dissolved in 15 ml. of 0.5% hydrochloric acid solution and made up to 50 ml. with distilled water. Application of the isatin reaction to a 1 ml. aliquot of this solution showed a recovery of 96.47% of the pyrrole.

Substances which interfere with the colour reaction may also, in some cases, be eliminated by extracting the pyrrole with ether. In order to effect a quantitative recovery, however, certain precautions must be taken which have not heretofore been recognized. The following experiment illustrates the procedure which the authors have employed successfully:— 10 ml. of a pyrrole solution containing 1.51 mg. of pyrrole was extracted by shaking with 10 ml. of ether in a small separatory funnel. The extraction was repeated five times and the extracts were combined. The ethereal solution was dropped slowly into a suction flask containing 10 ml. of 5% acetic acid solution which was placed in a beaker of warm water (50 to 60° C.) and connected to the suction pump through a trap which also contained acetic acid solution. When all the ether had evaporated, the acetic acid solutions in the trap and in the suction flask were combined and made up to 100 ml. with water. Colorimetric determination of the pyrrole contained in a 1 ml. aliquot of this solution showed 94% recovery, whereas in the absence of the trap the recovery was only 27%.

The methods described above have been successfully employed in the determination of pyrrole in the decomposition products of biological materials.

II. The Determination of Pyrrole in the Decomposition Products of Biological Materials

It has long been known that many biological materials, particularly proteinaceous substances, yield pyrrole by dry distillation. The amount of pyrrole obtainable by the dry distillation of various substances is shown in Table I. These determinations were carried out as follows:— A weighed sample, usually about 0.1 gm. of the dry, powdered substance was introduced into a soft-glass test tube (⅝ × 6 in.), and the centre of the tube, after being softened in a flame, was drawn out to a construction of about 5 mm. and bent at an angle of about 45°. The tube was held in a clamp so that its mouth was below the surface of 10 ml. of a 5% solution of acetic acid contained in a

TABLE I

SHOWING THE YIELD OF PYRROLE OBTAINED BY THE DRY DISTILLATION OF VARIOUS SUBSTANCES

Substance	Yield of pyrrole, %	Substance	Yield of pyrrole, %
Gelatin	1 201 ± 0 075*	Ammonium mucate	37 15
Casein	0 14	Proline	1 83
Gluten	0 18	Hydroxyproline	7 31
Gliadin	0 22	Arginine	Trace
Glutenin	0 16	All other amino acids found in proteins, and ammonium salts of these amino acids	Nil
Ovalbumin	0 13		
Lactalbumin	0 03		
Edestin	0 06		
Chlorophyll	Nil		

* *Nine determinations.*

30 ml. beaker. The material was heated, gently at first, and finally to redness by applying a micro flame to the rounded base of the test tube. Heating was continued until no more vapour distilled over. The delivery tube was severed just above the shoulder and used as a funnel to transfer the contents of the beaker to a 100 ml. volumetric flask. This was found to be the simplest and most efficient of the many types of distillation apparatus tried. The isatin colorimetric determination was made, in the usual manner, a 1 ml. aliquot of the final solution being employed. It was found necessary, however, to remove coloured impurities from the distillate. The solution could be decolourized without loss of pyrrole, with Lloyd's reagent, about 0.2 gm. being employed to remove the colour from 5 ml. of the distillate.

It was noted that the yield of pyrrole obtained by the dry distillation of various proteins (Table I) amounted to what might be expected from their proline and hydroxyproline content if, as was found to be the case, only these two amino acids yield pyrrole on dry distillation. From their proline and hydroxyproline content, and the yield of pyrrole obtained by the dry distillation of these amino acids, the amount of pyrrole obtained from a number of proteins can be accounted for (see Table II). This observation is substantiated by the finding that when a hydrochloric acid hydrolyzate of 500 gm. of gelatin was fractionated by the classical methods the pyrrologenic material was found in the proline-hydroxyproline fraction. This material showed the following properties:— it was not precipitated by basic lead acetate nor by phosphotungstic acid; it was soluble in hot absolute alcohol; and 12% of it was precipitated in alcoholic solution by cadmium chloride (proline fraction). The alcohol soluble material gave a negative reaction to Foulger's modification of Molisch's test (3).

TABLE II

SHOWING THAT THE YIELD OF PYRROLE OBTAINED BY THE DRY DISTILLATION OF SEVERAL PROTEINS IS ACCOUNTED FOR BY ASSUMING THAT ONLY THE PROLINE AND HYDROXYPROLINE, WHICH THEY CONTAIN, YIELD PYRROLE

	Pyrrole by distillation, %	Proline (6), %	Hydroxyproline (6), %	Pyrrole by calculation, %
Gelatin	1.20	9.5	14.1	1.20
Casein	0.14	9.0	0.2	0.17
Gliadin	0.22	13.2	—	0.24

Pieroni (4) and Roncato (5) have reported the presence of pyrrole among the hydrolytic products of glutenin and gliadin. Using the sensitive isatin test the authors have failed to detect any free pyrrole in the hydrolyzates when gluten, gliadin, or gelatin were digested with pepsin, trypsin, pepsin followed by trypsin, papain, 10 or 20% sodium hydroxide, 25% hydrochloric acid, or 25% sulphuric acid, nor was any pyrrole detected in the steam distillates of any of these hydrolyzates.

The authors have further examined the effect of several oxidizing agents on the yield of pyrrole obtained by the dry distillation of gelatin. The addition of ferric chloride failed to alter the yield, and no pyrrole was obtained when the dry distillation was carried out after the gelatin had been treated with sodium hypochlorite, hydrogen peroxide, or alkaline permanganate. However, it was found that sodium peroxide did markedly increase the amount of pyrrole obtained from gelatin (see Table III). In Table IV the effect of the addition of copper sulphate is shown. These experiments suggest that the hydroxyproline and proline molecules differ greatly in their susceptibility to oxidation. It would appear that with hydroxyproline the oxidation was too vigorous when copper sulphate and sodium peroxide were added together. Proline, on the other hand, is apparently more difficult to oxidize, since, when the copper sulphate was omitted, the sodium peroxide alone failed to bring about its oxidation to pyrrole.

TABLE III

THE EFFECT OF SODIUM PEROXIDE ON THE PRODUCTION OF PYRROLE FROM A GELATIN HYDROLYZATE

Weight of sodium peroxide added to 80 mg. of gelatin comminuted with 5 gm. of sand, gm.	0.25	0.50	0.50	0.50	1.00
Increase in yield of pyrrole, %	85	180	200	190	105

TABLE IV

THE EFFECT OF COPPER SULPHATE ON THE PRODUCTION OF PYRROLE

Composition of test	Yield of pyrrole, %
100 mg. gelatin + 1 ml. H_2O	0.93
100 mg. gelatin + 1 ml. H_2O + 0.5 gm. Na_2O_2	2.65
100 mg. gelatin + 0.5 gm. Na_2O_2 + 1 ml. 10% $CuSO_4$	2.00
10 mg. proline + 2 ml. H_2O + 0.5 gm. Na_2O_2	Nil
10 mg. proline + 2 ml. H_2O + 0.5 gm. Na_2O_2 + 1 ml. 10% $CuSO_4$	8.44
10 mg. hydroxyproline + 2 ml. H_2O + 0.5 gm. Na_2O_2	7.25
10 mg. hydroxyproline + 2 ml. H_2O + 0.5 gm. Na_2O_2 + 1 ml. 10% $CuSO_4$	3.25

Acknowledgment

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A NEW COLORIMETRIC METHOD FOR THE DETERMINATION OF HYDROXYPROLINE AND ITS APPLICATION TO GELATIN HYDROLYZATES[1]

By W. D. McFarlane[2] and G. H. Guest[3]

Abstract

Hydroxyproline is oxidized by sodium peroxide, if copper or cobalt is present, to give an unstable red chromogen which, in hot acid solution, can be condensed with isatin to form a stable red complex. The conditions are described which permit the direct application of this reaction to the quantitative estimation of hydroxyproline in acid or alkali hydrolyzates of gelatin. By this method moisture-free gelatin is found to contain 14 65% of hydroxyproline.

Introduction

An examination of the literature reveals that few colour reactions are available for the detection and determination of hydroxyproline. Morse (5) introduced a new colour reaction, namely, the production of a red colour when a solution of hydroxyproline is heated with sodium peroxide in the presence of methylhexylcarbinol. A quantitative procedure based on this reaction has not so far been evolved, and in the authors' tests the reaction has been found to take place with explosive violence. Lang (4) and Waldschmidt-Leitz and Akabori (6) have shown that hydroxyproline reacts with sodium hypochlorite to yield 80% of pyrrole. The latter can then be determined colorimetrically, with *p*-dimethylaminobenzaldehyde or isatin, in the steam distillate. The hydroxyproline content of gelatin as determined by this procedure is, however, only 8.9 to 9.4% which is very low when compared to the amount obtained by isolation methods, *i.e.*, 14.1% by Dakin (2) and 14.4% by Bergmann (1).

It has been demonstrated (3) that there is a marked difference in the susceptibility of proline and hydroxyproline to oxidation. The authors have also found that, if a solution of hydroxyproline is treated with sodium peroxide and dilute copper sulphate solution and the mixture acidified with hydrochloric acid, a red colour develops on heating the solution in a boiling water bath. This constitutes a sensitive test for hydroxyproline which is not given by any other amino acid, including proline. The reaction does not take place if the copper sulphate is omitted. A method for the determination of hydroxyproline, based on this reaction, is described herein; when applied to gelatin hydrolyzates it gives results in good agreement with the values obtained by isolation methods.

Experimental

The qualitative test for hydroxyproline is carried out as follows:— To 1 ml. of a hydroxyproline solution or gelatin hydrolyzate containing at least 0.5

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mg. of hydroxyproline is added approximately 0.25 gm. of sodium peroxide and 1 ml. of 0.02 *M* copper sulphate solution. When effervescence has ceased, the mixture is neutralized with 2 *N* hydrochloric acid solution, with phenolphthalein as an indicator, and then an excess of hydrochloric acid is added to give a final concentration of approximately 0.1 *N* acid. The solution is placed in a boiling water bath for a few minutes and a red colour develops.

When the copper sulphate is replaced with an equimolecular solution of ferric sulphate, nickelous sulphate, or manganous sulphate no colour develops, but, from a given amount of hydroxyproline, cobaltous sulphate produces about one-third of the colour intensity given by copper sulphate. If hydrogen sulphide is used to remove the copper, just before the solution is finally heated in the water bath, the red colour fails to develop. The chromogen is insoluble in ether; it is not precipitated by mercuric sulphate and it gives no colour with isatin until the mixture is heated, when a red colour develops which, for a given amount of hydroxyproline, is more intense and more stable than the red colour developed on heating with hydrochloric acid alone. The substance may possibly be a complex copper salt of a dipyrryl methene.

A study of this reaction to determine its value as the basis of a quantitative procedure showed:—

(a) The intensity and the shade of the red colour are influenced by factors which are difficult to control. If, however, the chromogen is condensed with isatin the red colour which now develops is stable, and the conditions under which the colour intensity is proportional to the concentration of hydroxyproline can be established.

(b) The absorption curve of the red colour shows a maximum at about 520 mu, so that the intensity can best be measured in the Evelyn photoelectric colorimeter by employing the 520 mu filter.

The absorption curve of the red colour, obtained by applying the reaction to a gelatin hydrolyzate, is identical with that of the red colour developed from hydroxyproline.

(c) The amount of copper sulphate influences the reaction. Maximum colour intensity is obtained, if the reaction is carried out, with a 0.01 *M* copper sulphate solution.

(d) The use of solid sodium peroxide gives variable results. This difficulty is overcome by using instead 1 ml. of 6% hydrogen peroxide and 1 ml. of 10% sodium hydroxide solution.

The effect of *(a)* the temperature and duration of the heating of the reaction mixture, *(b)* the concentration of hydrochloric acid and isatin, and *(c)* the temperature and time of heating on the development of the red colour, have been investigated. The optimum conditions are given in the following description of the method.

Description of the Method

To 1 ml. of a solution containing 0.2 to 1.6 mg. of hydroxyproline are added 1 ml. of 0.01 *M* copper sulphate solution, 1 ml of 10% sodium hydroxide solution, and 1 ml. of 6% hydrogen peroxide. The mixture is allowed to stand for five minutes, with shaking at frequent intervals. The test tube is then placed in a boiling water bath for five minutes, cooled in running water, and neutralized by the addition of 1.5 ml. of 2 *N* hydrochloric acid solution. The solution is next transferred to a 10 ml. glass stoppered graduated cylinder and diluted to the 10 ml. mark with distilled water. After thorough mixing, 1 ml. of this solution is transferred to another 10 ml. graduated, glass stoppered cylinder; 1 ml. of a freshly prepared 0 01% aqueous solution of isatin and 1 ml. of 2 *N* hydrochloric acid solution are added, and the mixture is placed in a boiling water bath for exactly three minutes. The cylinder is removed from the water bath, allowed to stand for five minutes, and then cooled under running water. Water is then added to the 10 ml. mark, and, after mixing, the red coloured solution is transferred to a colorimeter tube. The intensity of the colour is measured in the photoelectric colorimeter, using the 520 light filter.

The heating times mentioned above should be closely adhered to. The isatin solution should be not more than two days old, and in its preparation gentle warming may be employed to facilitate solution of the isatin. The centre-setting of the colorimeter was obtained by using a control solution prepared by the same procedures, but with the hydroxyproline omitted. In Fig 1 are shown the calibration data obtained with solutions containing varying amounts of hydroxyproline. The reaction conforms with Beer's law, the value of *K* being 0 3483 ± 0.0095 with a maximum deviation of 0.0166.

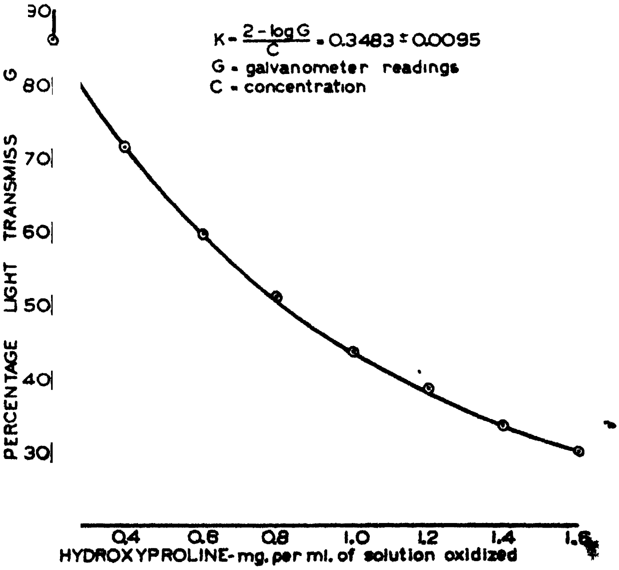

FIG. 1. *Showing the relation between the concentration of hydroxyproline and the intensity of the red colour.*

Application of the Method to Gelatin Hydrolyzates

Various methods of hydrolysis have been tested, with the results shown in Table I. In each case 0.5 gm. of finely powdered "Gold Label" gelatin, which analyzed 10.17% moisture and 17.46% nitrogen (moisture-free basis), was employed.

TABLE I

SHOWING THE RESULTS OF HYDROXYPROLINE DETERMINATIONS IN GELATIN HYDROLYZATES

Method of hydrolysis	Hydroxyproline, % of moisture-free gelatin
3 *N* HCl at 150° C. for three hours	14 19
3 *N* HCl at 150° C. for five hours	14 34
3 *N* HCl at 150° C. for six hours	14 53
3 *N* HCl at 150° C. for six hours	14 67
Saturated $Ba(OH)_2$ at 150° C. for three hours	13 07
Saturated $Ba(OH)_2$ at 120° C. for six hours	14 75

Hydrolysis was carried out in an autoclave at 150° C. and a pressure of of 70 lb., using 10 ml. of 3 *N* hydrochloric acid or 20 ml. of a saturated solution of barium hydroxide. At the completion of the acid hydrolysis the solutions were neutralized to a phenolphthalein end-point with sodium hydroxide, whereas the alkali hydrolyzates were neutralized by adding 5 ml. of 10% sulphuric acid to the hot solution. Each hydrolyzate was filtered into a 50 ml. volumetric flask and the precipitate on the filter paper washed with water until the total volume of the filtrate was 50 ml. The colorimetric determinations were carried out in duplicate, using 1 ml. aliquots of this solution. The "centre setting" of the colorimeter was obtained with a control solution which was prepared by treating 1 ml. of the hydrolyzate in the same way as the test solutions were treated, with the exception that it was not heated after addition of the isatin and hydrochloric acid solutions. This solution did not therefore develop a red colour, and it was used to compensate for the colour of the reagents

The three lowest results in Table I probably indicate incomplete hydrolysis, if these are omitted the mean value for the hydroxyproline content of gelatin becomes 14.65% (moisture-free basis). So far, the authors have been unable to detect hydroxyproline in casein, although the amount of the sample taken for analysis was such that hydroxyproline should have been detected if casein contains 0.2%.

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A NOTE ON THE COLORIMETRIC DETERMINATION OF PROLINE[1]

By G. H. Guest[2]

Abstract

A colorimetric method for the determination of proline is described. The procedure involves the oxidation of proline with lead peroxide and the condensation of the oxidation product with *p*-dimethylaminobenzaldehyde to give a red compound. The oxidation product can, if desired, be separated by steam distillation before applying the colour reaction. The method is limited in application to proteins which contain little or no hydroxyproline. By this method casein is found to contain 7.94% of proline.

Introduction

When a mixture of proline with sodium peroxide and copper sulphate is dry distilled, pyrrole is present in the distillate as indicated by a positive pyrrole-blue test with isatin (3). Proline or hydroxyproline, on oxidation with sodium peroxide in the presence of copper sulphate, gives oxidation products which react, in acid solution, with *p*-dimethylaminobenzaldehyde. The oxidation product of hydroxyproline, but not of proline, gives a red colour on condensing with isatin in acid solution (4). Determination of the relative intensity of the red colour produced, in the reaction with *p*-dimethylaminobenzaldehyde, from the same amount of proline and hydroxyproline under identical conditions, shows that 1 mg. of hydroxyproline produces the same intensity of colour as 10 mg. of proline. These observations suggested the possibility of evolving a method for determining proline and hydroxyproline in protein hydrolyzates. Such a procedure was worked out, but when it was applied to gelatin hydrolyzates the results were always much lower than those recorded in the literature and obtained by isolation methods (1).

It was considered that it would be necessary to separate the compound which produced the red colour with *p*-dimethylaminobenzaldehyde from interfering substances. The oxidation product of proline or hydroxyproline cannot be steam distilled nor can it be extracted with ether or precipitated with mercuric salts. It has been found, however, that lead dioxide will oxidize proline and hydroxyproline to products which give a red colour with *p*-dimethylaminobenzaldehyde and which are also volatile in steam.

After a careful study of the optimum conditions for the oxidation of proline by lead dioxide and for the colorimetric determination with *p*-dimethylaminobenzaldehyde, a procedure has been evolved for the determination of proline. This method has, so far, been found to be applicable only to proteins, such as caseinogen, which contain little or no hydroxyproline.

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Description of the Method

To 2 gm. of casein in a 50 ml. Erlenmeyer flask was added 40 ml. of a saturated solution of barium hydroxide. The flask was placed in an autoclave for three hours at 150° C. and a pressure of 70 lb. On removal of the flask from the autoclave 10 ml. of 10% sulphuric acid solution was added to the contents of the flask and, after cooling, the mixture was filtered into a 100 ml. volumetric flask. The residue was washed on the filter paper, with distilled water until 100 ml. of filtrate was collected.

A 5 ml. aliquot of the filtrate was neutralized to phenolphthalein with 1 *N* sodium hydroxide solution, and to it were added 5 ml. of water, 10 ml. of phosphate buffer (pH 8.7) and 1 gm. of lead dioxide. The mixture was refluxed for 30 min., cooled, filtered into a 200 ml. volumetric flask, the residue washed with water, and the filtrate finally made up to volume. To 5 ml. of this solution in a glass-stoppered graduated cylinder were added 5 ml. of water, 1 ml. of a 4% solution of *p*-dimethylaminobenzaldehyde in 95% alcohol, and 1 ml of 2 *N* hydrochloric acid. The mixture was heated in a boiling water bath for one minute, and cooled by allowing to stand for five minutes and then placing in cold running water. The colour intensity was measured in an Evelyn photoelectric colorimeter using the 520 mu light filter.

The proline equivalent was calculated by referring to a calibration curve which was prepared from the data obtained by applying the above reactions to amounts of proline varying from 1 to 5 mg. The colour reaction conforms with Beer's law, the mean value of K being 0 0578 ± 0 0020 with a maximum deviation of 0 0051.

This sample of casein was found to contain 7 94% proline (moisture-free basis) which is in close agreement with the value obtained by Dakin (2) by his butyl alcohol method.

It will be noted that, in the application of the method to casein, steam distillation was not employed. A slightly lower value for the proline content of casein is obtained if steam distillation is introduced, but in this particular case no advantage was found to accrue from its use. Smaller amounts of the protein may, of course, be employed.

Possibly the method can be modified to be applicable to proteins containing hydroxyproline so that hydroxyproline and proline may be simultaneously determined in the same hydrolyzate. However, circumstances have made it necessary that this investigation be discontinued for the present.

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NOTE ON PERSISTENCE OF LIQUID STRUCTURE IN THE CRITICAL REGION

Investigations carried out in this laboratory have shown that above the critical temperature, as defined by the temperature of the disappearance of the meniscus, a heterogeneity in a one component system persisted. By "molecular stirring", by heating the medium considerably above this temperature and then reproducing the original temperature, or by isothermal expansion, this heterogeneity disappeared and a homogeneous system was obtained which persisted indefinitely. Up till now it has been impossible to produce a heterogeneous system once the critical temperature, as defined above, has been passed. It is of considerable importance to record that this is possible.

The two phase system ethylene was heated to above the critical temperature and the expected heterogeneity recorded. It was then heated up five degrees above the critical and on cooling to the previously recorded temperature the system was homogeneous. By means of a heating jacket covering the upper portion of the bomb, the lower portion of the medium was subjected to pressure which was maintained for some time. The experimental arrangement was such that the whole system was immersed in a thermostat so that the lower portion of the medium remained at constant temperature. When the temperature of the jacket was allowed to fall to the thermostat temperature a heterogeneity persisted, i.e., the density of the lower portion of the medium reached an asymptotic value definitely higher than that of the upper portion. Such experiments have been found to give reproducible results, and it has therefore been shown that above the critical temperature it is possible to produce in a one component system a dense and a less dense medium apparently in equilibrium with each other. The inferences to be drawn are left to the detailed publication of the results of these experiments.

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THE ELECTROLYSIS OF SOME ORGANIC COMPOUNDS WITH ALTERNATING CURRENT[1]

BY J. W. SHIPLEY[2] AND M. T. ROGERS[3]

Abstract

The a-c. electrolysis of a number of organic compounds was carried out in order to ascertain what products might be obtained, what electrolytic conditions affected the nature and the yield of products, and to discover the general relations governing oxidation and reduction when a.c. is used. Oxidation was found to predominate over reduction, owing, probably, to the relatively low hydrogen overvoltage on the electrodes. The effect of varying the conditions of a-c. electrolysis was in general similar to that observed in d-c. electrolysis. Satisfactory yields were obtained only when a product of an irreversible process was concerned. A good yield of quinhydrone from the a-c. electrolysis of hydroquinone was secured at a relatively high current density. The chlorination of acetone by the a-c. electrolysis of a solution of acetic anhydride in hydrochloric acid gave a current yield of 35% at a current density of 2 amp. per cm^2.

Introduction

The alternating current electrolysis of water has been extensively studied by Shipley and Goodeve (15, 17, p. 3), and a theory developed which satisfactorily accounts for the decomposition of water into its elements. They showed that current density was the important factor in the electrolysis and that there exists a critical current density, specific for the electrode, below which no hydrogen or oxygen was evolved and above which these gases were given off in accordance with Faraday's law. The specific current density at which gases were evolved was shown to be a function of the capacity of the electrodes for storing hydrogen and oxygen.

The possibility of obtaining oxidation or reduction of organic compounds using a.c. was first shown by Drechsel (5, 6), who obtained a variety of products in small yield from the electrolysis of various organic compounds. Pearce and Couchet (13), using a.c., observed the reduction of nitrobenzene to aniline and found that high current densities were most favourable for reduction. Brochet and Petit (3, 4) found that non-reversible effects occurred on electrolyzing solutions of the salts of fatty acids, whereas Baur (1) observed that the products of a-c. electrolysis were frequently the same as those found for d-c. electrolysis but that the proportions differed. Leblanc and Schick (10, 11), from the results obtained by varying the frequency of alternation, calculated the duration of existence of organic radicals. Above a certain rate of alternation no product was observed. Fichter (8) found that in general, with an organic depolarizer, no compounds could be isolated using a.c. that are not obtainable with d.c. The only case observed and reported where a.c. gives a product not obtainable with d.c. is the solution of copper and other metals in potassium cyanide solutions (3, 4). The ions are removed as complexes when formed and, on the reversal of the current, the metals do not plate out.

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No quantitative data relating to the electrolysis of organic compounds by a.c. could be found in the literature, and few investigations of this subject have been reported in recent years. The present work was undertaken in an attempt to determine the general relations governing oxidation and reduction, to determine the behaviour of various types of organic compounds on electrolysis, and to find reactions suitable for quantitative study using a-c. electrolysis.

It was understood that, since oxidation and reduction alternated with each change of phase of the current, only the products of irreversible processes could be expected. Relatively insoluble, non-ionizing, complex and gaseous products might however be formed and be readily separated from the electrolyte and thus have a quantitative significance. Electrode material, electrolyte temperature, voltage, frequency, and current density are conditions that affect electrolysis. The effect of varying these conditions is recorded in the experimental work but, of course, relatively few of the possible combinations could be studied.

Little is known concerning the mechanism of electrolysis and the energy distribution between electrode and electrolyte when electron exchange takes place. An accumulation of facts in regard to a-c. electrolysis should be of some value in a study of this mechanism.

Experimental

The most efficient d-c. method modified for a-c. electrolysis was chosen, but much higher current densities and in most cases platinum electrodes were used. Other electrodes, with the exception of gold and carbon, are too severely corroded by electrolysis to be of general use. Platinum itself is somewhat attacked in almost all cases. The electrodes, of 1 sq. cm. area and covered at both ends with glass, consisted of two parallel wires, an arrangement providing uniform current density. Gold electrodes were provided by plating platinum wires, whereas silver and nickel wires and zinc sticks were used for electrodes of these metals. Graphite electrodes were cut from large electrodes. The electrode vessel was a glass tube of 150 cc. capacity immersed in an ice bath and provided with a motor stirrer. Gases off the electrodes were analyzed as follows:— carbon dioxide, oxygen, and unsaturated hydrocarbons by absorption in potassium hydroxide, pyrogallol, and fuming sulphuric acid, respectively; hydrogen and carbon monoxide by combustion over copper oxide at 300° C.; and saturated hydrocarbons by combustion with oxygen over mercury. After electrolysis the solutions were tested for the presence of primary alcohols, aldehydes, formic acid, and esters by standard qualitative methods.

A.c. taken from the 60 cycle, 110 volt circuit was regulated by resistances, and effective current voltages were measured with a-c. instruments checked against standards.

Fatty Acids and Their Salts

The a-c. electrolysis of the aliphatic acids and their salts gave products quite similar to those obtained by d-c. electrolysis. Oxidation predominates over reduction where both are possible. This is probably due to the low hydrogen overvoltages possible when a.c. is used. The ratio of ethane evolution to hydrogen evolution [ethane efficiency (9, p. 281)] was used as a measure of the relative oxidation-reduction processes when the conditions of electrolysis were varied. The solvent was water.

TABLE I

A-C. ELECTROLYSIS OF 5% POTASSIUM ACETATE. PLATINUM ELECTRODES. INFLUENCE OF CURRENT DENSITY ON ETHANE EFFICIENCY

Current density, amp. per cm^2.	1.0	3.0	5.0	7.0
Ethane efficiency, %	17.0	40.7	56.6	62.0
Oxygen in gas evolved, %	1.2	0.0	1.0	2.0

Increase in current density increases the ethane efficiency but changes the amount of oxygen evolved very little. Apparently the Kolbe synthesis (9, p. 279) is favoured by increase of current density, as is found to be the case in d-c. electrolysis.

TABLE II

A-C. ELECTROLYSIS OF POTASSIUM ACETATE. PLATINUM ELECTRODES. INFLUENCE OF CONCENTRATION (CURRENT DENSITY, 7 AMP. PER CM^2.)

Concentration, in gm. per 100 cc. water	50.0	7.5	0.75
Ethane efficiency, %	62.0	42.4	0.0
Oxygen in gas evolved, %	2.0	1.4	20.0

Increase in concentration gives a higher yield of ethane, and less oxygen is evolved, as in d-c. electrolysis. An increase in temperature was also found to lower the ethane efficiency and increase the production of oxygen. This also occurs in the d-c. electrolysis.

Varying the concentration of potassium acetate did not affect the ethane efficiency of the electrolysis appreciably, but in a neutral solution the efficiency dropped. Thus at a current density of 4 amp. per cm². it was found to be but 16% instead of about 48%.

Nickel and silver electrodes favoured the production of hydrogen; no ethane was detected. Carbon electrodes produced mostly hydrogen and carbon dioxide, with a little ethane, and there was disintegration of the electrodes. Iron and zinc electrodes evolved hydrogen only and the electrodes disintegrated. These results indicate that with nickel, iron, and zinc electrodes no appreciable oxidation occurs.

The addition of potassium carbonate and potassium bicarbonate to the acetate electrolyte inhibited the production of ethane. Methanol in appreciable amount was detected in the electrolyte, hence it is probable that the Hofer-Moest reaction (9, p. 285) replaces the Kolbe synthesis.

A saturated solution of potassium acetate in anhydrous acetic acid, when electrolyzed with a.c. at platinum electrodes and at a current density of 0.6 amp. per cm²., gave an ethane efficiency of 40%. Ethane was also evolved at mercury electrodes but with lower efficiency.

Electrolysis of Potassium Propionate

A 30% solution of potassium propionate containing 2% of propionic acid was electrolyzed with a.c., and the results shown in Table III were obtained.

TABLE III

Electrolysis of potassium propionate

Electrodes	Amp. per cm.²	Per cent CO_2	Per cent O_2	Per cent H_2	Per cent hydrocarbons	
					Unsat'd	Sat'd
Platinum	0.5	30.0	4.2	53.8	5.6	6.2
Platinum	1.5	31.5	3.5	47.6	12.5	2.8
Platinum	2.7	35.1	1.2	43.4	17.9	3.6
Platinum (alkaline sol'n)	3.0	4.7	6.6	68.0	19.2	1.2
Carbon (acetic sol'n)	1.2	36.3	1.0	36.0	19.6	3.8

The oxidation increases somewhat with current density (percentage of carbon dioxide rises), and the amount of ethylene produced also increases with the current density, whereas the production of butane and oxygen decreases. The reactions concerned are probably:

$$2\ C_2H_5COO^- + H_2O_2 \longrightarrow C_4H_{10} + 2\ CO_2 + 2\ OH^-$$
$$2\ C_2H_5COO^- + H_2O_2 \longrightarrow C_2H_4 + C_2H_5COOH + CO_2 + 2\ OH^-$$
$$2\ C_2H_5COO^- + H_2O_2 \longrightarrow C_2H_5COOC_2H_5 + CO_2 + 2\ OH^-$$

the second reaction, producing ethylene, being favoured by increase of current density. The products are similar to those found in d-c. electrolysis (9, p. 300).

A-c. Electrolysis of Potassium Butyrate and Potassium n-Caproate

A saturated solution of potassium butyrate, slightly acid with butyric acid, on a-c. electrolysis using platinum electrodes and a current density of 1 amp. per cm². gave the following products:

Per cent CO_2	Per cent O_2	Per cent CO	Per cent H_2	Per cent hydrocarbons	
				Unsat'd	Sat'd
28.7	1.3	0.6	57.6	8.9	0.8

A relatively large amount of primary alcohol remained in the electrolyte, together with some esters and a trace of aldehydes. The isopropyl alcohol probably arose from the hydrolysis of propylene and the hexane by a reaction similar to that producing butane in the electrolysis of potassium propionate.

A saturated solution of *n*-potassium caproate electrolyzed with platinum electrodes at a current density of 3 amp. per cm². gave a relatively large yield of esters and alcohols, with about a 5% current efficiency yield of decane.

The Kolbe synthesis seems to occur with a-c. electrolysis of the paraffin series just as it does with d.c.

A-c. Electrolysis of Ethyl Alcohol and n-Propyl Alcohol

A solution containing 50 gm. of ethyl alcohol, 3 gm. of sulphuric acid, and 150 cc. of water was electrolyzed, platinum gauze electrodes and a current density of 3 amp. per cm². being used; temperature, 40° to 50° C. A current yield of 2.5% acetaldehyde and 8.0% acetic acid was obtained. It was hoped that a-c. electrolysis might give a higher yield of aldehyde than d.c., but this was not the case. The a-c. electrolysis of *n*-propyl alcohol gave a current yield of 17% propionic acid.

Aromatic Hydrocarbons

A 10% suspension of benzene in 100 cc. of 4% sodium sulphate was electrolyzed at 20°, with platinum gauze electrodes, at a current density of 2 amp. per cm². and with stirring. A current yield of about 1% hydroquinone was obtained. Maleic and formic acids were found, as well as other breakdown products, but most of the current is lost by the production of hydrogen and oxygen. Benzene, being insoluble in the electrolyte, is a very inefficient depolarizer. D-c. electrolysis of benzene produces quinone but with a.c. the quinone is reduced to hydroquinone on successive alternations of the current.

An emulsion of *p*-xylene in 10% sulphuric acid containing acetone (to dissolve it) was electrolyzed in a manner similar to that used for benzene but at a current density of 20 amp. per cm². The products sought were *p*-tolualdehyde and *p*-toluic acid. It was thought that the intensity of oxidation might be moderated to favour the accumulation of aldehyde, but a current yield of only 5% aldehyde and about 1% *p*-toluic acid was obtained. Fichter (8) found 26% aldehyde and 6.4% acid as the current yield for d-c. electrolysis.

Aniline

The a-c. electrolysis of aniline in hydrochloric acid solution gave a fair current yield of aniline black. Oxidation rather than chlorination took place, since no chlorination product was detected.

Hydroquinone

A 6% solution of hydroquinone in water, to which was added a little sulphuric acid, was electrolyzed at platinum electrodes, a current density of 3 amp. per cm^2. being used. A current yield of 50% of green-black, crystalline, almost pure, quinhydrone was obtained. This a-c. electrolysis was studied in detail in order to find the operating conditions for obtaining maximum yield. A following paper records the results.

Thiourea

A-c. electrolysis of thiourea, 3 gm. in 100 cc. of 6 *N* hydrochloric acid, at current density of 2 amp. per cm^2., temperature 20° C., and treatment of the products of electrolysis with a saturated potassium nitrate solution at 0° C., gave a 13% current efficiency for oxidation, the product being $C_2H_6N_4S_2 . 2HNO_3$ (dithio formamidine dinitrate). The use of sulphuric acid in place of hydrochloric acid and treatment of the electrolyte with ethyl alcohol gave a 15% current yield of $C_2H_6N_4S_2 . H_2SO_4$. The polymerized oxidation product in neither case is reduced readily at platinum electrodes, nor is it very susceptible to further oxidation. The above yields are lower than those obtained in d-c. electrolysis.

Polymerization of Thiosulphate

A 20% solution of sodium thiosulphate was electrolyzed with platinum electrodes, and a series of determinations were made over a range of current densities. The sodium thiosulphate oxidized was determined by titration with iodine solution before and after the electrolysis. At a current density of 2 amp. per cm^2. the current efficiency for oxidation to S_4O_6 was 57%, but on increasing the current density above this value the yield progressively fell off. This result was not expected, but it may be explained by assuming that at high current densities hydrogen peroxide is formed in high concentration and much of it decomposes to give oxygen before S_2O_3 can diffuse in to react with it. There is also probably a high local heating effect at the electrode at higher current densities which will favour the decomposition of hydrogen peroxide and the evolution of oxygen.

Oxidation of Oxalate

The a-c. electrolysis of a saturated solution of sodium oxalate containing 5% sulphuric acid gave a marked increase in the production of carbon dioxide as the current density increased. The efficiency of the oxidation at a current density of 2 amp. per cm^2. was 9.34%; at 3 amp. per cm^2., 17.6%; and at 6 amp. per cm^2., 29.4%.

Electrolysis of Acetone

Fifty grams of acetone in 200 cc. of 5% sulphuric acid was electrolyzed at platinum gauze electrodes with a current density of 1.0 amp. per cm^2. After passage of 30 amp.-hr. no pinacol could be detected in the electrolyte, but such oxidation products as formic and acetic acids were identified. An analysis of the gases evolved indicated that a complex electrolytic process had occurred in which oxidation had predominated.

Ammonium Thiocyanate

The a-c. electrolysis of ammonium thiocyanate was carried out, by an adaptation of the d-c. process described by Perkin (14), using 15 gm. of ammonium thiocyanate in 200 cc. of water and 20 cc. of concentrated hydrochloric acid as electrolyte, platinum electrodes, and a current density of 2 amp. per cm^2. Canarine, being insoluble, separated out but in a current yield of about one-third that obtained by d-c. electrolysis.

Potassium Ethyl Malonate

A concentrated solution of potassium ethyl malonate was prepared by saponifying diethyl malonate with the calculated amount of potassium hydroxide in ethyl alcohol. The solution was electrolyzed by a.c. in an apparatus similar to that used for acetates. No diethyl succinate could be isolated. This negative result was expected since the product is stable towards reduction and, if formed, would not be reduced.

Substitutions

(A) Chlorination of Acetone

Acetone (130 cc.) dissolved in 100 cc. of concentrated hydrochloric acid and kept below 35° C. was electrolyzed by a.c. at platinum gauze electrodes, without stirring, and a current density of 2.0 amp. per cm^2. A yellow oil separated, and after the passage of 35 amp.-hr. this oil was collected and fractionated. A 35% current yield of monochloroacetone was obtained. A variety of other chlorination products also resulted but no oxygen was evolved. The platinum electrodes dissolved slowly.

(B) Iodoform from Ethyl Alcohol

The preparation of iodoform by the method of Muller (12) was attempted by the use of a-c. electrolysis, but the results were not encouraging. The current efficiency at a current density of 2 amp. per cm^2. was only 5%.

(C) Iodination of Thymol

The method used was an adaptation of that described in a patent by Bayer and Co. (7). Thymol in 200 cc. of water containing 7 gm. of potassium iodide and 1 gm. of sodium hydroxide was electrolyzed at platinum electrodes with a current density of 1.5 amp. per cm^2. Because the product, di-thymol di-iodide, is insoluble, it was hoped that a.c. would give a satisfactory yield, but a current yield of only about 1% was obtained. Apparently the oxidation of thymol occurred as indicated by the evolution of carbon dioxide.

Other Reactions Studied

(A) o-Nitrobenzoic Acid

Shipley and Calhoun (16) obtained a 92% yield of anthranilic acid on the reduction of *o*-nitrobenzoic acid by d-c. electrolysis. Using a.c. and platinum electrodes in an alcoholic solution containing sulphuric acid, the authors obtained only tars and resins, and no amines could be detected. Apparently at current densities between 2 to 3 amp. per cm^2. the oxidation is too intense for the production of amines.

(B) Reduction of Pyridine to Piperidine

Since piperidine is not readily oxidized to pyridine it seemed probable that this reduction might be obtained with a.c. Both platinum and zinc electrodes were used but only traces of piperidine could be found after the passage of 20 amp.-hr. The gases evolved contained 3% of carbon dioxide and 17.5% of oxygen; this indicated some complete oxidation.

(C) Reduction of Nitrates

The a-c. electrolytic reduction of potassium nitrate to potassium nitrite, using zinc and iron electrodes, mechanical stirring, and an ice cooled electrolyte, gave good results. The following data show the variation of the efficiency of reduction with current density, using zinc electrodes.

Current density, amp. per cm^2.	0.5	1.0	5 0	6.0
Reduction efficiency, %	16.4	18.4	38.8	44 0

(D) Reduction of Ethyl Benzoate

No ethyl tolyl ether was obtained in the attempted a-c. reduction of ethyl benzoate, using platinum and mercury electrodes. Mercury is an unsuitable electrode material because of its rapid corrosion and the production of salts of mercury.

Discussion

The nature of the products from the electrolysis of organic compounds with a sine wave a.c. has been determined for a number of typical compounds. Electrodes of platinum, gold, and carbon were found to be the most satisfactory. Nickel may be used in alkaline solution. Electrodes of the baser metals are unsuitable, as they are severely corroded and the products interfere with the electrolysis.

Oxidation was found to predominate over reduction where both were possible. With noble metal electrodes this might be expected, as they have relatively low-hydrogen overvoltages, and a.c. will further tend to reduce the amount of reduction by preventing the hydrogen overvoltage from building up to a value high enough to bring about reduction of the organic compound.

Bowden and Rideal (2) showed that a finite time is required for either the oxygen or hydrogen overvoltage to rise to its full value, when the current is reversed. In many cases this time was less than the total wave for a 60 cycle current; thus both reduction and oxidation would be moderated because the overvoltage of hydrogen and oxygen would be lower than the maximum during most or all of the half-wave. A high hydrogen overvoltage is usually required for efficient reduction, so the absence in all cases of any appreciable reduction with a.c. was to be expected (nitrate to nitrite in 44% yield at zinc electrodes, current density 6 amp. per cm^2., was the greatest yield obtained).

In the case of oxidation the problem in d-c. electrolysis is usually to moderate the oxidation and prevent it resulting entirely in the production of carbon dioxide and water. An a.c. might therefore be expected to be as efficient as d.c., and in certain reactions, even superior. Only in the case of oxidation of hydroquinone to quinhydrone at high current densities was this observed.

Most halogen substitution reactions consist of two separate processes—the discharge of the halogen ion and the substitution of a hydrogen atom of the organic compound by the halogen.

When the electrode is anode, an a.c. discharges the halogen ion, and, provided that the organic depolarizer can remove it sufficiently rapidly so that none is left to again take on an electron on the reversal of the current, the efficiency of a substitution reaction should be relatively high. This was found to be the case when a 35% current yield of chloroacetone was obtained in the a-c. electrolysis of acetone in concentrated hydrochloric acid.

As both oxidation and reduction occur at an electrode, the oxidation or substitution product must not be readily susceptible to reduction, or appreciable amounts would be unable to accumulate. Thus iodoform, which is rather easily reduced at a platinum cathode, gave a current yield of about 5%. Similarly a reduction product would have to be stable to oxidation to be present in good yield. This is rarely the case.

A method to prevent the oxidation of the reduced molecule is to use base metal electrodes. The hydrogen overvoltage is relatively high, so reduction is favoured, and, when the electrode becomes anode, the solution of the metal as a cation occurs rather than the alternative process—the oxidation of the compound. This was utilized in the reduction of nitrates to nitrites at zinc electrodes.

Relatively stable oxidation products, such as quinhydrone or dithioformamidine, or gases as in the case of ethane, ethylene, carbon dioxide, or insoluble compounds as in the case of aniline black, (a solid) and $C_{10}H_{22}$ (liquid). were isolated in appreciable yields by a-c. electrolysis.

Soluble compounds with soluble oxidation and reduction products, as in the case of ethyl alcohol and *p*-nitrobenzoic acids, gave mixtures of compounds all unpromising in yield as far as a method of their preparation was concerned. The yields with a.c. were in all cases but one (that of hydroquinone) less than with d.c. There are several reasons for this. Irreversible losses of current occur owing to the capacity of the electrodes for storing electrolytic products. Reversal of the electrolytic action of one wave will occur when alternation of the current takes place. Also there is a portion of the time in which the potential of the electrodes is below the decomposition potential of the electrolyte, as the e.m.f. passes through zero twice in each wave. This portion will be negligible at high potentials but is appreciable when the potential is low.

Only for a very few reactions is it to be expected that a.c. will be of use in favouring a desired product or in increasing yield over that given by d-c. electrolysis. At high current densities, however, it will usually maintain and often increase yields, thus enabling high current densities to be efficiently used. This is illustrated above in the a-c. electrolysis of potassium acetate.

The effect of various factors on the yield of products by a-c. electrolysis depends on the nature of the reaction. Usually these factors are the same for d.c. and a.c. Thus, for the oxidation of acetates, the effect of various factors may be explained on the basis of the hydrogen peroxide theory of Glasstone and Hickling (9, p. 251). The results found by the present authors indicate that increase of current density increases ethane efficiency. As a higher concentration of hydrogen peroxide would follow increase of current density, more rapid oxidation of the acetate ion would be expected. The rate of increase in yield falls off at high current density, since acetate ions do not diffuse in rapidly enough to react with the oxygen formed from the decomposition of hydrogen peroxide. Increase of acetate concentration increases the efficiency of ethane production because acetate ions are supplied in greater concentration for the reaction with hydrogen peroxide. The presence, in large concentration, of ions foreign to the reaction, as in the experiment in which potassium bicarbonate and potassium carbonate were added, causes a lowering of the relative concentration of acetate ion, and methanol formation replaces ethane formation [the Hofer-Moest reaction (9, page 285 *et seq.*)]. Higher temperatures lower the ethane efficiency and increase oxygen evolution since hydrogen peroxide is more unstable at high temperatures. Electrodes which are good catalysts for peroxide decomposition also lower the yield. Platinum gave the highest yield of ethane, carbon much less, and nickel, lead, zinc, and iron gave none.

An indeterminate effect no doubt influencing electrolysis is that of a high local heating on the surface of the electrode. This will be almost independent of the temperature of the electrolyte, and arises in part from the recombination of products at the electrode surface. It is not unlikely that the presence of methane in the products of the electrolysis of potassium acetate in anhydrous acetic acid results from the pyrolysis of ethane on the electrode surface. The effect of this local heating on the electrolysis has not been determined.

The control of a reaction is often possible in d-c. electrolysis by careful preparation of the electrode surface. This is not practicable in a-c. electrolysis, as all forms of the same electrode material acquire the same surface a short time after the electrolysis begins.

A low current density usually is most efficient with d.c. since the oxygen or hydrogen is in low concentration over the surface of the electrode, and the depolarizer can be provided in sufficient concentration to react rapidly enough to prevent the evolution of oxygen or hydrogen, as the case may be. The existence of a capacity for electrolytic products on the electrodes necessitates, in nearly all cases, a relatively high current density (usually greater than 0.3 amp. per cm^2.) in order to obtain any net oxidation and reduction. Hence high current densities are desirable. For reactions of the type of the oxidation of acetate, in which a high concentration of active oxygen or hydrogen peroxide at the electrode raises the efficiency of oxidation, higher current densities increase the yield. This increase is limited only by the concentration of depolarizer, the rate of diffusion, and the ease with which the depolarizer is oxidized. The oxidation of $S_2O_3^{=}$ to $S_4O_6^{=}$ was found to decrease with increase of current density, probably owing to the above conditions not being fulfilled.

Recombination of evolved gases was observed in nearly all cases in which platinum electrodes were used. This recombination took place not only in the gas above the electrolyte but also in the electrolyte itself. The latter was indicated by an elevation of the current density at which evolution took place.

This recombination was assumed to be due to the catalytic action of platinum black.

An examination of the experimental results shows that a-c. electrolysis proceeds, in general, so far as the final products are concerned, in a manner similar to d-c. electrolysis, but that oxidation is favoured over reduction. Only a few of the reactions studied indicated that a-c. electrolysis might be expected to give yields comparable to d-c. electrolysis. These are the oxidation of hydroquinone to quinhydrone, the production of ethane by the electrolysis of potassium acetate in aqueous and in acetic acid solution, the chlorination of acetone, and the polymerization of thiosulphate to tetrathionate. Two of these reactions have been studied in detail and the results will appear in a following paper.

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NOTE ON THE MOUNTING OF SMALL METAL SPECIMENS IN RESIN PLAQUES

In the preparation of very small specimens of metal for polishing, etching, and metallographic examination, it was found that they could be mounted conveniently by embedding in discs of a thermoplastic synthetic resin. Samples weighing only 1 or 2 mg. were mounted in this way.

The resin was a commercial polystyrene of melting point 175 to 185° C. Its transparency is an advantage in this work. A small electrically heated screw press and a positive cylindrical mold were used. The granular resin was first molded into a disc 1 in. in diameter and $\frac{1}{2}$ in. thick, a pressure of 1000 lb. per sq. in. at a temperature of 125° C. being applied.

The specimen was placed centrally on the disc and both were returned to the mold. The plunger of the mold was placed on the specimen and heat and pressure were applied as before. The resulting piece contained the metal sample firmly embedded and flush with the surface.

FIG. 1. *Metal flakes.* × *250.*

A photomicrograph of a mounted specimen, after polishing and etching, is shown in Fig. 1.

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RECEIVED 22 DECEMBER, 1938.

THE NITRATION OF *m*-DICHLOROAZOXYBENZENE AND THE REDUCTION OF SOME OF THE PRODUCTS[1]

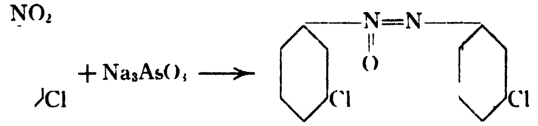
By H. E. Bigelow[2] and W. H. Steeves[3]

Abstract

The nitration of *m*-dichloroazoxybenzene and the fractional crystallization of the nitrated products is described. Evidence for the structural formula of each is given. The reduction of some of the nitro derivatives with sodium arsenite to form azobisazoxy and trisazoxy compounds containing chlorine is also discussed.

Introduction

The usual method of nitrating azoxy compounds is by treatment with concentrated or fuming nitric acid according to the number of nitro groups desired. This method was used in nitrating *m*-dichloroazoxybenzene which was prepared by reducing *m*-nitrochlorobenzene with sodium arsenite in an alkaline solution of sodium hydroxide, a new method for its preparation.



After refluxing the *m*-dichloroazoxybenzene with concentrated nitric acid, a reddish oily substance was obtained. Steam distillation of this product gave a pale yellow oil having a boiling point ranging from 75° to 235° C. No further investigation has yet been made of this oil. The solid residue, however, was subjected to a long series of fractional crystallization from which five compounds were obtained: *(A)* m.p. 116°; *(B)* m.p. 145°; *(C)* m.p. 112°; *(D)* m.p. 105°; *(E)* m.p. 157° C. All were yellow needles of different shades varying from a greenish yellow to an orange yellow. All except *(E)* were found, on analysis, to be mononitro derivatives of *m*-dichloroazoxybenzene, *(E)* being a dinitro derivative.

The determination of the structure of these compounds rests upon the established fact that substitution in the ring adjacent to the oxygen atom attached to the nitrogen of the azoxy group by a semi-polar double bond never occurs (1, p. 128). The assumption is therefore made that all substitution takes place in the one ring. To determine their structural configuration these substitution products, where possible, were reduced to the corresponding amines with scission of the azoxy-linkage. Where the amines had already been prepared the structure followed at once. In most cases, unfortunately, the amines have not yet been prepared.

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[1] *Manuscript received January 9, 1939.*
Contribution from the Department of Chemistry, Mount Allison University, Sackville, New Brunswick, Canada.

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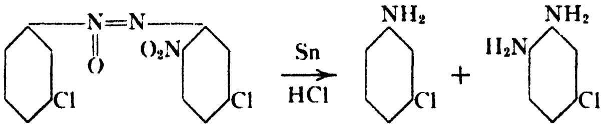
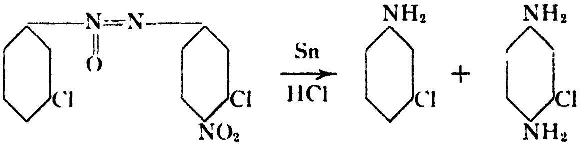
[3] *Demonstrator, Department of Chemistry, Mount Allison University, 1932-1933. Present address; Mount Allison University, Sackville, N.B.*

Reduction of these compounds to their corresponding amines showed that *(A)* was *o*-nitro-*m*-dichloroazoxybenzene, and *(B)* was *p*-nitro-*m*-dichloroazoxybenzene. Neither sodium amalgam nor tin and hydrochloric acid could reduce *(C)* to the corresponding amine. Instead, a white flaky compound, m.p. 169° C., resembling a hydrazo compound was obtained. However, since it has been impossible to nitrate more than one benzene ring of azoxy compounds, this is probably the other ortho derivative rather than meta, as it was found in fairly large quantity. *(D)* was found in very small quantity. Consequently no structural investigation of it has yet been made. It is, however, probably the meta derivative which would be formed in small quantity.

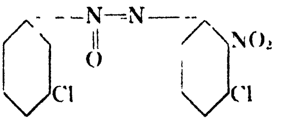
(A) m.p. 116°



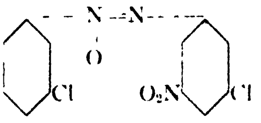
(B) m.p. 145°



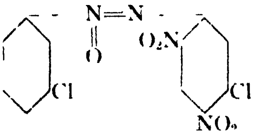
(C) m.p. 112°



(D) m.p. 105°



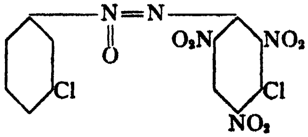
(E) m.p. 157°



(E) was the only dinitro derivative found. Since the ortho and para positions of *m*-dichloroazoxybenzene are occupied most readily by nitro groups as indicated by the fact that, of the mononitro derivatives, *(A)* and *(B)* were found in larger quantities, the above structural formula is probably correct.

Nitration with Fuming Nitric Acid

When *m*-dichloroazoxybenzene was refluxed with fuming nitric acid two trinitro derivatives were obtained, *(F)* m.p. 182° C. and *(G)* 165° C. One would expect the compound found in larger quantity *(G)* to be symmetrical and have the formula

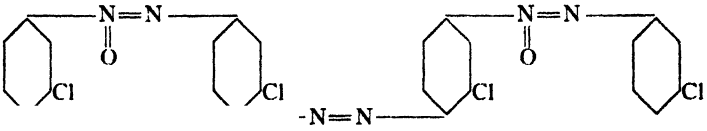


because the nitro groups would substitute ortho and para to the groups already present, and meta to one another. Further evidence for this structure for *(G)* lies in the fact that *(G)* was obtained by treating either *(A)* or *(B)* with fuming nitric acid. Thus far it has been impossible to determine with certainty the structure of these two trinitro derivatives of *m*-dichloroazoxybenzene, since they are not acted on by reducing agents such as tin and hydrochloric acid under ordinary conditions. These compounds, if reduced to aryl amines, would give amines which, as yet, have not been prepared. In consequence they have not been further studied.

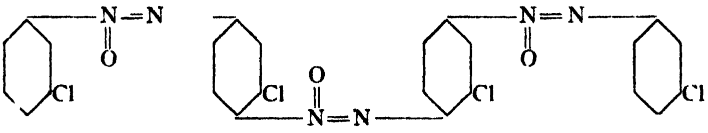
Sodium Arsenite Reduction of Nitro Derivatives

Reduction of *p*-nitro-*m*-dichloroazoxybenzene *(B)* with sodium arsenite gave *(H)* the azobisazoxy and *(I)* the trisazoxy derivatives of *m*-dichloroazoxybenzene.

(H)



(I)



The tetrachloroazobisazoxybenzene *(H)*, m.p. 210° C., was brick red in colour, while the tetrachlorotrisazoxybenzene (*I*) was bright yellow, m.p. 195° C. The latter was obtained in small quantity.

So exceedingly stable was *(H)* that it could not be oxidized to the azoxy derivative *(I)* by 90% hydrogen peroxide in glacial acetic acid. It is interesting to note that azobisazoxybenzene is oxidized by peracetic acid with ease to trisazoxybenzene (5, p. 122).

The sodium arsenite reduction of *o*-nitro-*m*-dichloroazoxybenzene *(A)* gave a gelatinous compound *(J)* which was crystallized from water. It exploded before melting at 275° C., contained no chlorine, formed a hydrochloride, m.p. 178° C., and was extremely explosive. The structure of this compound has not yet been determined.

Experimental

Preparation of m-Dichloroazoxybenzene

A paste of arsenic trioxide (76 gm.) and water was poured with continuous stirring into a solution of 100 gm. of sodium hydroxide. To this solution was added 72 gm *m*-chloronitrobenzene. The mixture, in a two litre, three-necked, round bottom flask with 250 cc. water, was stirred for six hours at 104° C. An amount of water was then added sufficient to prevent sodium arsenate from precipitating on cooling. Dark yellow crystals of *m*-dichloroazoxybenzene, which separated on cooling, were filtered, dried, and crystallized from alcohol; m.p., 97° C. Yield, 85%.

Nitration of m-Dichloroazoxybenzene

To *m*-dichloroazoxybenzene (56 gm.) was added 250 gm. of concentrated nitric acid (sp. gr. 1.45) and the mixture refluxed for six hours. The dark red viscous oil obtained was steam distilled. The distillate contained a small amount of pale yellow oil which was found to have a boiling point ranging from 75° to 235° C.

Experience showed that one of the compounds in the residue after steam distillation was quite insoluble in cold benzene, the others were very soluble, and that this fact made possible the isolation of *(A)* for further purification. Accordingly the residue after steam distillation was crystallized from benzene by cooling with ice, filtered, and further purified by crystallizing from benzene until the melting point of the pale yellow crystals became constant at 116° C. Calcd. for *(A)* $C_{12}H_7O_3N_3Cl_2$: Cl, 22.73%; M.W., 312. Found: Cl, 22.58%; M.W., 310.

Separation by Fractional Crystallization

The mother liquor from *(A)* was evaporated on a steam bath and the residue was subjected to a long series of fractional crystallization from an equal mixture of benzene and alcohol. Four compounds were obtained having constant melting points in the following order: *(B)* 145°; *(C)* 112°; *(D)* 105°; and *(E)* 157° C. All of these compounds crystallized in yellow needles of different shades, and all except *(E)* were found on analysis to be mononitro derivatives of *m*-dichloroazoxybenzene. *(E)* was found to be a dinitro derivative. *(A)* and *(B)* were obtained in fairly large quantities, about 20% each, *(C)* about 4%, and *(D)* and *(E)* in very small quantities—less than 1%. Calcd. for *(B)* $C_{12}H_7O_3N_3Cl_2$: Cl, 22.73%. Found: Cl, 22.46%. Calcd. for *(C)* $C_{12}H_7O_3N_3Cl_2$: Cl, 22.73%. Found: Cl, 22.70%. Calcd. for *(D)* $C_{12}H_7O_3N_3Cl_2$: C, 46.15; H, 2.46; Cl, 22.73%; M.W., 312. Found: C, 46.16; H, 2.83; Cl, 22.48%; M.W., 313.7. Calcd. for *(E)* $C_{12}H_6O_5N_4Cl_2$: N, 15.69%; Found: N, 15.75%.

Reduction of (A), m.p. 116° C., with Tin and Hydrochloric Acid

The reduction of this compound took place with difficulty forming tarry materials and yielding only a very small quantity of the corresponding amines.

Five grams *(A)* was reduced with tin and hydrochloric acid at room temperature over a period of seven days. The resulting mixture was made basic, extracted with ether, and crystallized from benzene and ligroin. *m*-Chloraniline was obtained along with a small amount of yellow crystals, m.p. 73 to 76° C., that of 4-chloro-1,2-diaminobenzene (3, p. 555; 4, p. 773). This established the structure of *(A)*.

Reduction of (B), m.p. 145° C., with Tin and Hydrochloric Acid

In the presence of alcohol and water *(B)* was reduced with tin and hydrochloric acid. After heating on a steam bath for two hours, the mixture was poured into an excess of 20% sodium hydroxide. The base was extracted with ether, evaporated, and crystallized from benzene and ligroin. *m*-Chloraniline was obtained along with yellow crystals having constant m.p. 63° C., that of 2-chloro-1,4-diaminobenzene (2). Evidently compound of m.p. 145° C. was *p*-nitro-*m*-dichloroazoxybenzene.

Reduction of Compound (C), m.p. 112° C., with Tin and Hydrochloric Acid

This compound, as has already been stated, gave a white flaky material having m.p. 169° C. when reduced with tin and hydrochloric acid. On analysis this product showed that the reduction was incomplete and suggested some type of hydrazo derivative. Other reducing agents were used but so far it has been impossible to reduce the compound to the amine.

Nitration with Fuming Nitric Acid

m-Dichloroazoxybenzene (50 gm.) was refluxed for two hours with 200 gm. of fuming nitric acid. The resulting mass was poured into water and neutralized with sodium bicarbonate. The solid yellow product was subjected to a series of fractional crystallizations from an equal mixture of alcohol and benzene. Two trinitro derivatives were obtained, *(G)* m.p. 165° C. and *(F)* m.p. 182° C. *(G)* appeared first and was obtained in larger quantity. When crystallizations were made from benzene alone, *(F)* appeared first. *(G)* was also obtained by nitrating either of the mononitro derivatives *(A)* or *(B)*. Calcd. for *(F)*, trinitro derivative, $C_{12}H_5O_7N_5Cl_2$: C, 35.8; H, 1 24; Cl, 17.6%; M.W., 402. Found: C, 36 8; H, 1.25; Cl, 17.2%; M.W., 400.9. Calcd. for *(G)*, trinitro derivative, $C_{12}H_5O_7N_5Cl_2$: Cl, 17.62%; M.W., 402. Found: Cl, 17.69%; M.W., 401.

Preparation of Azobisazoxy and Trisazoxy Derivatives

The reduction of *p*-nitro-*m*-dichloroazoxybenzene (*B*) with sodium arsenite was brought about by adding 6 gm. of *(B)* to a solution of 15 gm. of arsenic trioxide, 20 gm. of sodium hydroxide in 100 gm. of water, and 25 gm. of alcohol. The mixture was refluxed and stirred with a mechanical stirrer in a three necked flask for two hours. A reaction took place causing the mixture to turn a deep red suggesting an azo compound. Before cooling, 300 gm. of water was added to keep the sodium arsenate in solution. After cooling, the mixture was filtered, dried, and crystallized from benzene. The brick coloured mass was recrystallized from benzene until the melting point became constant at 210° C. This, on analysis, was shown to be *m*-tetrachloroazobisazoxybenzene. Calcd. for $C_{24}H_{14}O_2N_6Cl_4$: Cl, 25.36%. Found: Cl, 25.33%.

From the crude benzene mother liquors of the azobisazoxy derivatives was isolated a small quantity of pale yellow crystals having m.p. 195° C. A micro analysis of this compound showed it to be *m*-tetrachlorotrisazoxybenzene. Calcd. for $C_{24}H_{14}O_3N_6Cl_4$: N, 14.58%. Found: N, 14.33%.

Reduction of o-Nitro-m-dichloroazoxybenzene (m.p. 116° C.)

The sodium arsenite reduction of this compound did not take place in the usual manner. Neither an azobisazoxy nor a trisazoxy compound was formed. Instead a water soluble product was obtained which was extremely explosive on heating and which formed a well defined hydrochloride with m.p. 178° C. It is hoped that in the near future the structure of this highly explosive compound will be determined.

Acknowledgment

The authors wish to express their thanks to Dr. R. Morehouse who prepared Compound B.

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THE PRODUCTION OF ETHANE, QUINHYDRONE, AND POTASSIUM CUPRIC CYANIDE BY A-C. ELECTROLYSIS[1]

By J. W. Shipley[2] and M. T. Rogers[3]

Abstract

The quantitative production of ethane, quinhydrone, and potassium cupric cyanide by a-c. electrolysis was studied in respect to conditions affecting yield. It was found that a good yield (about 90%) of quinhydrone was obtained by a-c. electrolysis, at low frequency and moderately high current density, of an aqueous solution of hydroquinone. This method of preparation has a distinct advantage in respect to space-time yield over the method of d-c. electrolysis. The current yield of potassium cupric cyanide at low current density (0.3 to 1.0 amp. per cm.^{2}) using a.c. was in the neighbourhood of 88%. A-c. electrolysis was not found to indicate any particular advantage over d-c. electrolysis, as far as could be ascertained by comparing the ethane efficiency of the two processes.

Introduction

An investigation by the authors (5) on the electrolysis of some organic compounds by a.c. made it desirable to obtain quantitative data in respect to the conditions affecting the yield of products of certain typical reactions. The reactions chosen were the production of ethane, quinhydrone, and potassium cupric cyanide. It was thought that a study of the conditions affecting yield of product might shed some light on the mechanism of electrolysis and indicate whether a-c. electrolysis might have some specific effect not secured by d.c.

The rate and efficiency of production as a function of current density and frequency were determined, tabulated, and compared graphically.

Experimental

The apparatus for electrolysis and analysis was the same as that described in the preceding paper (5).

THE OXIDATION OF POTASSIUM ACETATE

Potassium acetate was electrolyzed in aqueous solution and in anhydrous acetic acid over a range of current densities. The same concentration of acetate, 50% by weight, was used in all determinations in aqueous solutions and a saturated solution of acetate in anhydrous acetic acid as non-aqueous electrolyte.

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[1] *Manuscript received December 16, 1938.*
Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta.

[2] *Professor of Chemistry, University of Alberta.*

[3] *Tegler Research Fellow, University of Alberta.*

Table I contains the data for the a-c. electrolysis of potassium acetate in aqueous solution. Ethane efficiency is the ratio of the volume of ethane to that of hydrogen produced, while the rate of ethane production is expressed in cc. per min.

TABLE I

OXIDATION OF POTASSIUM ACETATE IN AQUEOUS SOLUTION. TEMP. = 12 TO 15° C.
SOLUTION: 50% POTASSIUM ACETATE, 5% ACETIC ACID

Current density, amp. per cm.^{2}	H_2, %	O_2, %	C_2H_6, %	Rate of evolution of C_2H_6, cc. per min.	Ethane efficiency, %
1	58.8	0.2	10.0	0 2	17.0
2	57.0	0.0	16.2	3.2	27.5
3	53.5	0.0	21.8	6.6	40.7
4	51.9	0.0	23.0	10.0	44.3
5	49.2	1.0	25.8	15.2	52.4
6	48.0	1.3	26.7	20.7	55.6
7	40.0	2.0	24.8	27.3	62.0
8	52.2	2.0	33.0	33.0	63.3

Table II gives the data for the a-c. electrolysis of potassium acetate in anhydrous acetic acid.

TABLE II

ELECTROLYSIS OF POTASSIUM ACETATE IN ANHYDROUS ACETIC ACID. TEMP. = 25° C.
ELECTRODES, SMOOTH PLATINUM

Current density, amp. per cm.^{2}	Rate of gas evolution, cc. per min.	H_2, %	C_2H_6, %	Rate of evolution, of C_2H_6, cc. per min.	Ethane efficiency, %
0.57	0.30	43.7	13.4	0.04	
1.0	3.1	36.1	21.5	0.62	59.6
1.2	6.4	33.7	23.2	1.5	68.8
1.5	8.0	35.6	26.0	2.08	73.0
1.9	9.4			2.45	
2.5	22.6	33.8	25.7	5.8	76.0
3.2	40.0	31.3	24.7	9.88	79.0
3.5	47.0			11.7	

Because of the high resistance of the electrolyte higher currents could not be used.

OXIDATION OF HYDROQUINONE

(a) A saturated solution of hydroquinone in water at 0° C. was used. About 30 cc. of 6 *N* sulphuric acid was added per litre to make the solution conducting. The electrolytic solution was cooled in ice, and platinum wire electrodes were used. The quinhydrone was obtained by cooling the solution to 0° C., at which temperature it is very slightly soluble, filtering off the precipitate on a tared filter, washing with water, drying, and weighing. This was repeated over the range of current densities from the decomposition point of 0.5 amp. per cm.^{2} to 10 amp. per cm.^{2}

A series of determinations was also made at frequencies of 20 and 30 cycles at current densities up to 6 amp. per cm.[2]

These frequencies were obtained by means of a Westinghouse motor-generator set using a separately excited armature and field. The frequency was calculated from the speed of the generator.

(b) The procedure of *(a)* was repeated using gold electrodes prepared by plating platinum with gold.

(c) Corresponding data were obtained using d.c.

The data are collected in Tables III to VI.

TABLE III

ELECTROLYSIS OF HYDROQUINONE

Electrodes, smooth platinum. Frequency, 60 cycles

Current density, amp. per cm.^{2}	Yield of quinhydrone, gm. per min.	Rate of gas evolution, cc. per min.	CO_2, %	O_2, %	O_2, cc. per min.	Amp. per min. used to produce O_2
0.03	0.0045					
0.5	0.0008					
1	0.01	3.0	0.3	1.2		
2	0.03	5.6				
3	0.08	11.3	0.3	1.3	0.14	0.04
4	0.15	16.3	0.5	1.6	0.25	0.07
5	0.20	23.5				
6	0.26	32.2	0.6	1.8	0.58	0.10
7	0.35	39.0	0.8	2.0	0.78	0.40
8	0.38	45.5	1.3	2.8	1.23	0.50
9	0.41	54.6	1.3	4.8	2.60	0.73
10	0.45	58.8	1.0	6.0	3.53	1.0

TABLE IV

ELECTROLYSIS OF HYDROQUINONE

Gold electrodes. Frequency, 60 cycles

Current density, amp. per cm.^{2}	Yield of quinhydrone, gm. per min.	Rate of gas evolution, cc. per min.	CO_2, %	O_2, %	O_2, cc. per min.	Amp. per min. used to produce O_2
1		1.6				
1.2	0.009					
2	0.040		0.4	0.6		
2.5	0.070					
3	0.112	12.05	0.0	2.0	0.25	0.07
3.5	0.163				0.54	
4	0.185	18	0.1	3.0	0.54	0.15
4.5	0.216					
5	0.230	25.6	0.3	3.8	0.97	0.27
6	0.265	29.5	0.7	4.8	1.41	0.40
7	0.315	40.0	1.1	6.0	2.40	0.67
8	0.370	46.2	1.5	6.5	3.0	0.84
9	0.410	55.2	2.0	8.1	4.5	1.26
10	0.450					

TABLE V

ELECTROLYSIS OF HYDROQUINONE. DIRECT CURRENT

Current density, amp. per $cm.^2$	Yield of quinhydrone, gm. per min.	
	Platinum electrodes	Gold electrodes
0.15	0.006	
1	0.06	
2	0.106	0.12
4	0.21	0.22
5		0.27
6	0.35	0.32
7	0.39	0.37
8	0.42	0.41
9	0.44	0.44
10	0.45	0.50

TABLE VI

ELECTROLYSIS OF HYDROQUINONE WITH DIFFERENT ELECTRODES AND FREQUENCIES

Current density, amp. per $cm.^2$	Yield of quinhydrone, gm. per min.		
	Au electrodes, 20 cycles	Pt electrodes, 30 cycles	Pt electrodes, 20 cycles
0.5			0.011
1	0.041	0.025	
1.5			0.07
2		0.085	
2.5		0.115	0.13
3	0.165		
3.3			0.18
3.87		0.190	
4.5		0.235	0.26
5	0.285		
5.5			0.285
6	0.356		
7			0.31

It is seen from the above that decrease in frequency increases the yield, and that gold electrodes give a slightly better yield than platinum.

Influence of Other Factors on Yield of Quinhydrone

Effect of Added Ions

Various ions which might act as oxygen carriers were added, *e.g.*, CrO_4^{--}, Mn^{++}. They caused no change in the yields. Ions such as Na^+ and Ca^{++}, had no effect.

Influence of Temperature

Below 40° C., temperature was found to have but a slight effect on yield. Above 40° C., a distinct lowering of yield occurred with rise in temperature.

Influence of Electrode Material

The results for gold and platinum are in general similar. Gold gives a slightly higher yield over the range 0 to 5 amp. per cm.^{2} at 60 cycles, but at 20 cycles the yields are nearly the same. Silver, nickel, and iron electrodes dissolve in the solution, and no quinhydrone is formed. Carbon is quite efficient, the yields being comparable to those given by gold and platinum. Owing to the difficulty of determining surface area exactly, comparison is impracticable.

Influence of Acid Concentration

The concentration of sulphuric acid was found to have but a small effect on yield at 25° C. However, low concentrations give a high resistance electrolyte, and the resultant heating lowers the yield.

Phase Difference

To determine whether capacitance had any effect on the phase relations of current and e.m.f., an oscillograph was connected in the circuit. At all frequencies (60 cycles and lower) and current densities (0.5 amp. per cm.^{2} and higher) used there was no phase angle.

Decomposition Potentials

A cell containing 40% potassium acetate solution in water with 1% acetic acid was used at 20° C. Platinum electrodes were introduced as previously described. These gave a uniform current density and their area was known. The potential was slowly raised and the current and potential at the decomposition point observed, this point being taken as that at which bubbles of gas were first evolved continuously. After some time the electrolyte became warm and platinum black formed. The evolution then ceased, and increasing potentials were required to evolve gas. There was therefore no definite reproducible value of decomposition potential. With 50% potassium acetate and 0.7 volts the first evolution of gas occurred at a current density of 0.27 amp. per cm.^{2} This gives the intercept of the ethane-evolution curve on the current axis (see Fig. 1).

With a saturated solution of potassium acetate in glacial acetic acid the current density at which bubbles are first continuously evolved is 0.31 amp. per cm.^{2}. This gives the intercept on the current density axis in Fig. 1. For the determination of the potential at which quinhydrone is first formed, a saturated solution of hydroquinone in 0.1 *M* sulphuric acid was used. The first crystals of quinhydrone were observed at a potential of 1.2 volts and a current density of 1.35 amp. per cm.^{2} With d.c., 0.67 volts is the potential at which quinhydrone forms first.

The values of current plotted against potential gave, in all cases observed, a curve without a sharp break such as is noted with d.c. There appears to be no a-c. analogue of the d-c. decomposition potential.

Figs. 1, 2, 3, and 4 show the relation of rate of production with a-c. electrolysis to that required by Faraday's law.

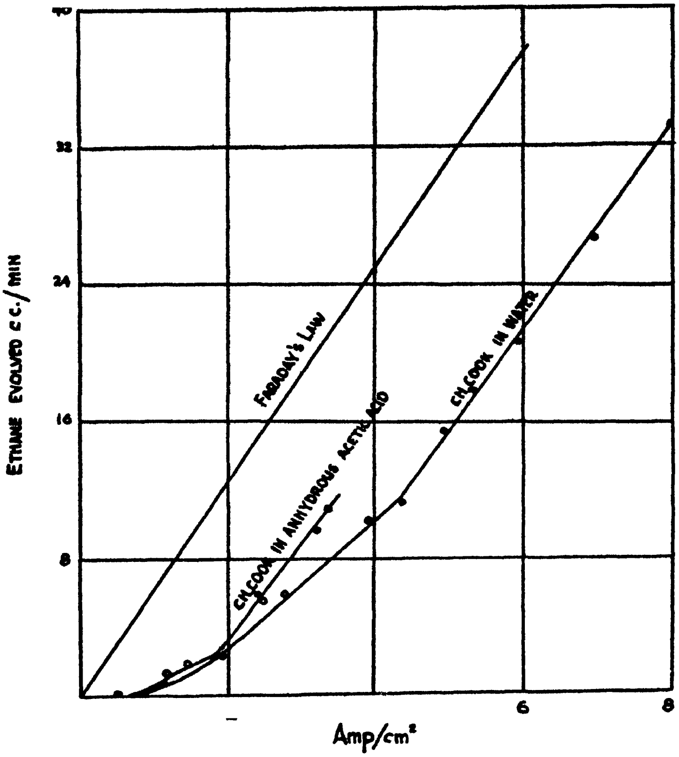

FIG. 1. *The rate of production of ethane from potassium acetate at platinum electrodes.*

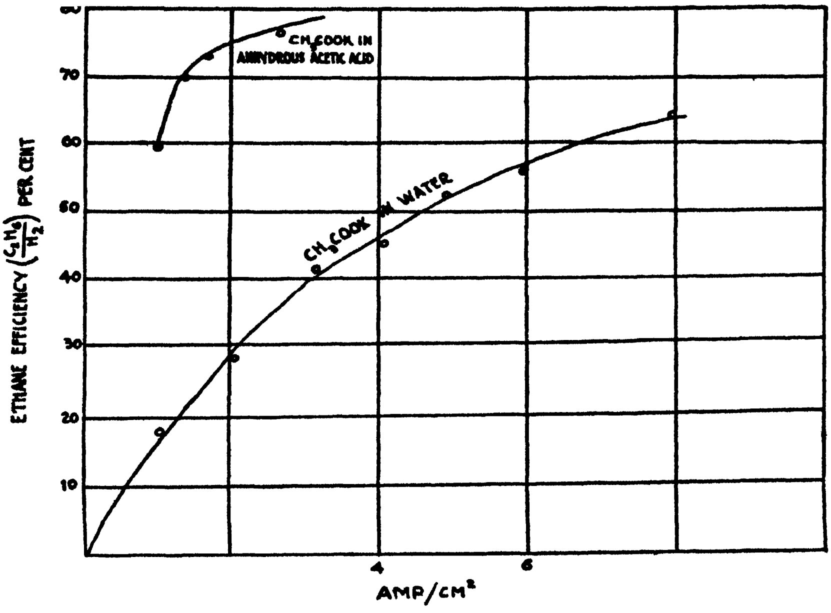

FIG. 2. *The variation of the efficiency of ethane production with current density.*

The Influence of Current Density on the Solution of Copper Electrodes in Potassium Cyanide

In order to obtain some knowledge concerning a reaction in which the formation of a complex ion is the irreversible process in electrolysis, the formation of potassium cupric cyanide by the a-c. electrolysis of an aqueous solution of potassium cyanide was studied, copper electrodes being used.

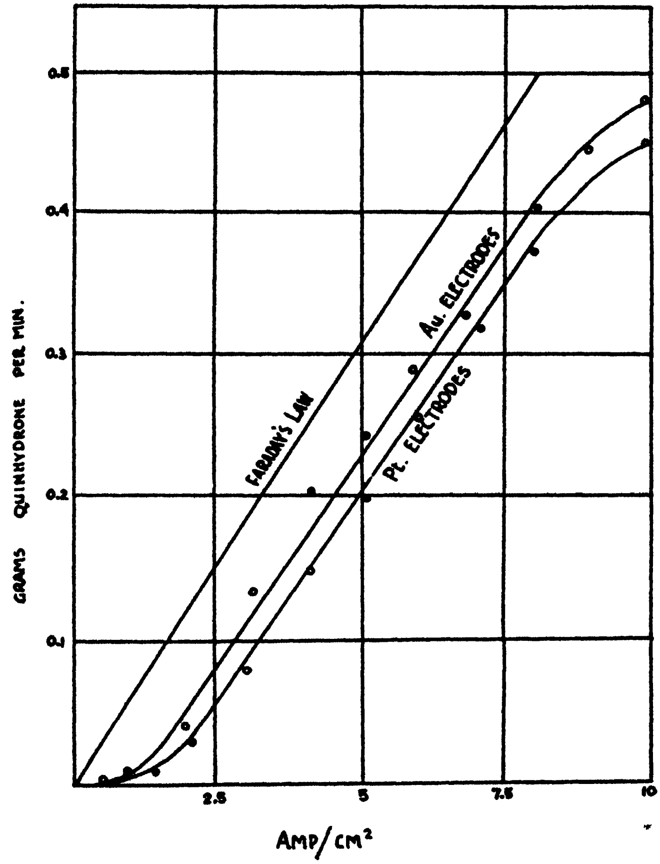

FIG. 3. *The rate of production of quinhydrone at platinum and gold electrodes with 60 cycle a.c.*

The reaction

$$2Cu + 8KCN + 2H_2O + 2e \longrightarrow 2K_3Cu(CN)_4 + 2KOH + H_2$$

takes place with a.c. since the copper ions first formed are removed as the complex cyanide, from which they are electrolytically deposited only with difficulty (2).

The influence of current density on this reaction was determined by passing an a.c. between weighed copper electrodes in 4 *N* potassium cyanide solution. After a known quantity of electricity had passed, the electrodes were dried and weighed. The current efficiency of the reaction for the solution of copper was calculated from the loss in weight of the electrodes. The results are shown in Table VII.

TABLE VII

CURRENT EFFICIENCY

Current density, amp. per cm.^{2}	0.05	0.3	0.7	1.0	1.75	2.0	3.0
Current efficiency of process, %	84.1	89.2	87.2	88.2	66.6	38.0	30.8

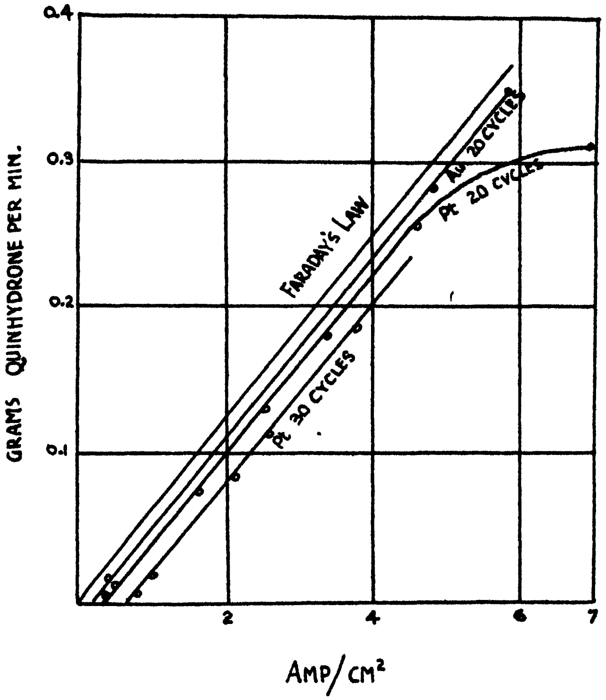

FIG. 4. *The rate of production of quinhydrone at platinum electrodes at frequencies of 20 and 30 cycles, and at gold electrodes at 20 cycles.*

No carbon dioxide was evolved and the percentage of oxygen was always less than 1. Thus, up to a value of 1 amp. per cm.^{2} the current density has little effect on current efficiency. At current densities higher than this the efficiency decreases rapidly. It may be assumed that at high current density the number of copper ions formed is greater than the number that can be removed as complexes in the time before the sign of potential of the electrode changes. The copper ions so remaining will be at once reduced to copper when the electrode becomes cathode. If the copper ions are not removed when the electrode becomes cathode, the copper will be electrolytically deposited. The reaction above is of a nature different from that of the reactions previously considered. This reaction is independent of current density until high current densities are reached, when copper ions are supplied more rapidly than they can be removed.

The results with iron electrodes were similar to those obtained with copper. Stirring was found to increase the yield at high current densities, a result expected from the above theory, and therefore confirming it.

Discussion

The three electrolyses studied in detail gave the same general results. At low current densities (below 0.5 amp. per cm.^{2}) the yield of products was very small. The best yields with d.c. are usually obtained at current densities lower than the above value. A-c. electrolysis apparently gives a relatively rapidly increasing yield of products over a range of current densities from the decomposition potential up to the point at which the rate of increase is in conformity with Faraday's law (see Fig. 3). It will be seen from this figure that, although the yield of products in this range is in conformity with that required by Faraday's law, they differ by a constant value. Thus, above a certain definite current density [critical current density—(3, 4, p. 3)], all additional current produces electrolytic products at a rate in accordance with Faraday's law.

This suggests that some constant factor, such as the capacity of the electrodes to hold electrolytic products, must be involved in the a-c. electrolysis of organic compounds.

Fig. 1 shows that after a current density of 4 amp. per cm.^{2} was reached the production of ethane became progressively greater with increase in current density in accordance with that required by Faraday's law. This indicated that the capacity of the electrodes for holding electrolytic products has become constant, and that electrolysis is proceeding as though but one determinate reaction was occurring. If more than one electrolytic reaction influencing the production of ethane were taking place, it could not be expected that this rate would be parallel with the rate of production required by Faraday's law.

In the case of potassium acetate in anhydrous acetic acid the only theory to account for the production of ethane is the discharged ion theory of Brown and Walker (1), and no chemical oxidation can occur. According to this theory the acetate ions are discharged at the anode; two free radicals then combine and decompose to give the products:

$$2CH_3COO^- \longrightarrow 2CH_3.COO + 2e$$
$$2CH_3COO \longrightarrow C_2H_6 + 2CO_2.$$

If the mechanism of electrolysis is of this nature, it might be expected that, since the discharged radicals take a finite time to decompose, some may not have decomposed when the current reverses. When the electrode becomes cathode, electrons are supplied and the radical would take up an electron. This would correspond to a decreased yield of ethane. The electrode would at the same time absorb hydrogen formed by discharge of hydrogen ions. On reversal of the current this hydrogen would be removed by oxidation or by the reverse process to give hydrogen.

$$H_2 \rightleftarrows 2H \qquad H \rightleftarrows H^+ + e.$$

At current densities greater than 2 amp. per cm.^{2} the curve for potassium acetate in anhydrous acetic acid (Fig. 1) becomes parallel to that required by Faraday's law, but is displaced from it by a constant current density. This indicates that the ratio of the current, represented by the sum of the current used to remove hydrogen absorbed on the electrode plus that used by a discharged radical in again taking up an electron, to the current represented by a half-wave of a-c. current, has become constant. The curve for ethane production therefore is parallel to that required by Faraday's law at current densities above 2 amp. per cm.^{2} The curves for hydrogen and oxygen production by the a-c. electrolysis of water (3, p. 325), were also found to depart in a similar manner from those required by Faraday's law. This was accounted for by assuming that the storage capacity of the electrodes for electrolytic gases decreased with the area of the half-wave below a certain current density. If this is the explanation of the observed curvature at low current densities, the same explanation applies to the curvature, at low current densities, of all the curves in Figs. 1, 3 and 4. It is obvious that a lower storage capacity for electrolytic products on the electrodes will leave a greater proportion of the total quantity of electricity in the half-wave available for the oxidation and reduction of the depolarizer (organic or inorganic).

The curves for the oxidation of hydroquinone in Fig. 3 are similar to the curves for ethane production included in Fig. 1, except that at high current densities the curves depart from parallelism with Faraday's law. It was found from the gas analysis data in Table I that oxygen evolution increased rapidly at high current density, and that this increase corresponded to the increase of curvature in the quinhydrone production curves of Fig. 3. This indicates that oxygen evolution partly replaces oxidation of hydroquinone to quinhydrone at high current density. Complete oxidation of hydroquinone did not occur to any appreciable extent, as shown by the absence of maleic acid in the analysis, and therefore the curvature was not due to complete oxidation of the benzene ring. At current densities above 7 amp. per cm.^{2}, the percentage of carbon dioxide in the gas evolved indicates that some complete oxidation had occurred.

The portion of the quinhydrone production curve parallel to that required by Faraday's law indicates that over this range of current densities the storage capacity of the electrodes for hydrogen and oxygen (3, 4, p. 3) is similar to that in the a-c. electrolysis of water. At high current densities it is probable that the storage capacity of the electrodes for hydrogen and oxygen remains unchanged, but hydroquinone does not diffuse to the electrode rapidly enough to accept all the oxygen produced by the discharge of the hydroxyl radical, and therefore oxygen is evolved.

The area of the half-wave representing a.c. decreases with increasing frequency. The ratio of the current not used in the oxidation of hydroquinone (owing to the capacity of the electrode for storing hydrogen and oxygen) to the total current passing, represented by the half-wave, will increase with increasing frequency (3, p. 317). Therefore the yield of quinhydrone at low frequencies will be greater, as was found experimentally.

The portion of the production curves which parallels those given by Faraday's law gives a measure of the yield to be expected as a function of current density. It is probable that a study of other a-c. electrolytic reactions might show but a short range where this parallelism occurs, and significant yields as a function of current density would not be indicated. At very high current densities the depolarizer could not be supplied to the electrode rapidly enough, and oxygen and hydrogen evolution from aqueous solutions, and alternative oxidation and reduction processes when organic solvents are used, would occur. For example, when the acetate ion cannot be supplied rapidly enough to the electrode, oxidation of acetic acid to methanol may occur rather than the Kolbe synthesis producing ethane.

Current yields of quinhydrone greater than 90% were obtained at low frequencies and moderately high current densities. Corresponding yields with d.c. were obtained only at very low current densities. Thus the a-c. production of quinhydrone would be found advantageous in respect to space-time yield. The possible advantage of a-c. production over d-c. is that the high yields are obtained at high current densities. Also, the alternation of current favours the diffusion of depolarizer to the electrode surface, and tends to give a higher current efficiency for the products.

An indeterminate factor in a-c. electrolysis is the effect of local heating on the electrode surface.

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FURTHER OBSERVATIONS ON THE DETERMINATION OF PHOSPHATE BY PHOTOELECTRIC COLORIMETRY[1]

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Abstract

A study of factors affecting the ceruleomolybdate reaction for phosphate is reported. The concentrations of stannous and stannic ions, the presence of extraneous salts, and temperature are important factors affecting the intensity and stability of the blue colour.

The stannous chloride reagent should be preserved from oxidation by storing it under hydrogen.

The interference by ferric iron is due largely to its reaction with the reducing agent, and may be avoided by diluting the sample to contain 0 1 p.p.m. of phosphorus and using two or three times the usual quantity of stannous chloride.

The method for the determination of phosphate recently described (3) in a communication from this laboratory has been in constant use since that time in studies of soil phosphorus relationships. Certain difficulties have been encountered which have led to further investigation of the factors influencing the development and stability of the ceruleomolybdate colour. This article is intended to amend and supplement certain of the data reported in the previous paper.

Effect of Stannous and Stannic Ions

In the earlier work the recommendations of Truog and Meyer (9) with regard to the concentrations of the reagents were adopted. The effect of stannous chloride was investigated (3) on the unwarranted assumption that the stannous chloride used to prepare the 2.5% reagent was pure. The use of a new lot of stannous chloride in the preparation of the reagent resulted in a considerable increase in the calibration constant, and also gave an appreciable colour in the control solutions. Analysis of the two lots of stannous chloride by iodimetric titration, according to Scott (6), but without reduction of the stannic ion, showed only 32.4% of stannous tin in the old sample, as compared to 93.8% stannous tin in the new sample. In terms of a 2.5% solution of stannous chloride the effective concentrations were 0.81 and 2.37% respectively.

The effect of the new stannous chloride on the rate and extent of colour development was investigated. Different amounts of stannous chloride, as indicated in Table I, were added to 10 ml. aliquots of phosphate solutions containing acid molybdate, and the colour development was followed by means of the Evelyn colorimeter. A series of results is given in Fig. 1. The curves show that the concentration of stannous ion exerts a very considerable influence

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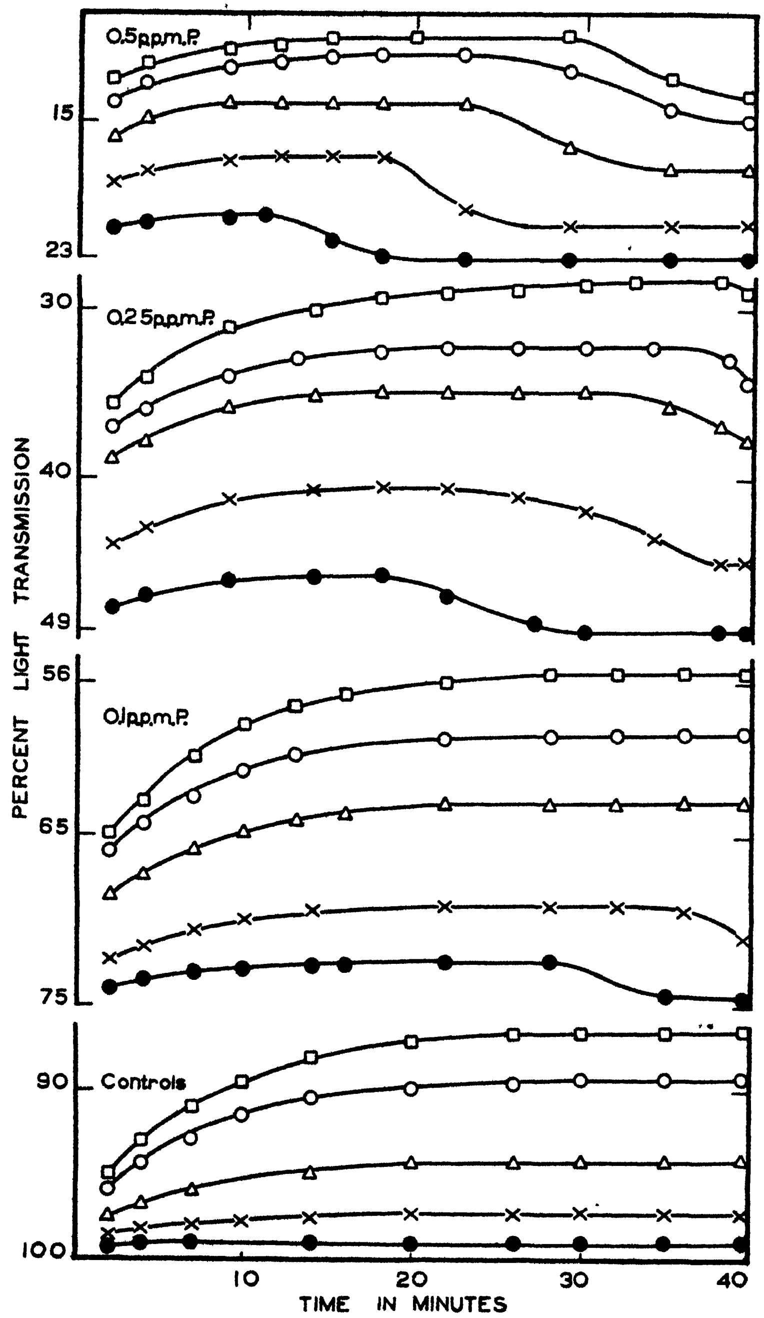

FIG. 1. *The influence of stannous chloride on the development and stability of the blue colour.* ● *1 drop of 1%* $SnCl_2 . 2H_2O$; × *1 drop of 2%* $SnCl_2 . 2H_2O$; △ *1 drop of 3%* $SnCl_2 . 2H_2O$; ○ *1 drop of 4%* $SnCl_2 . 2H_2O$; □ *1 drop of 5%* $SnCl_2 . 2H_2O$. (*21 drops equal 1 cc.; temperature of all solutions, 23.5° C.*)

on the colour development, since an increase in its amount results in an increase in the maximum colour intensity, and also increases the time required before the maximum is reached, and the length of time for which the colour

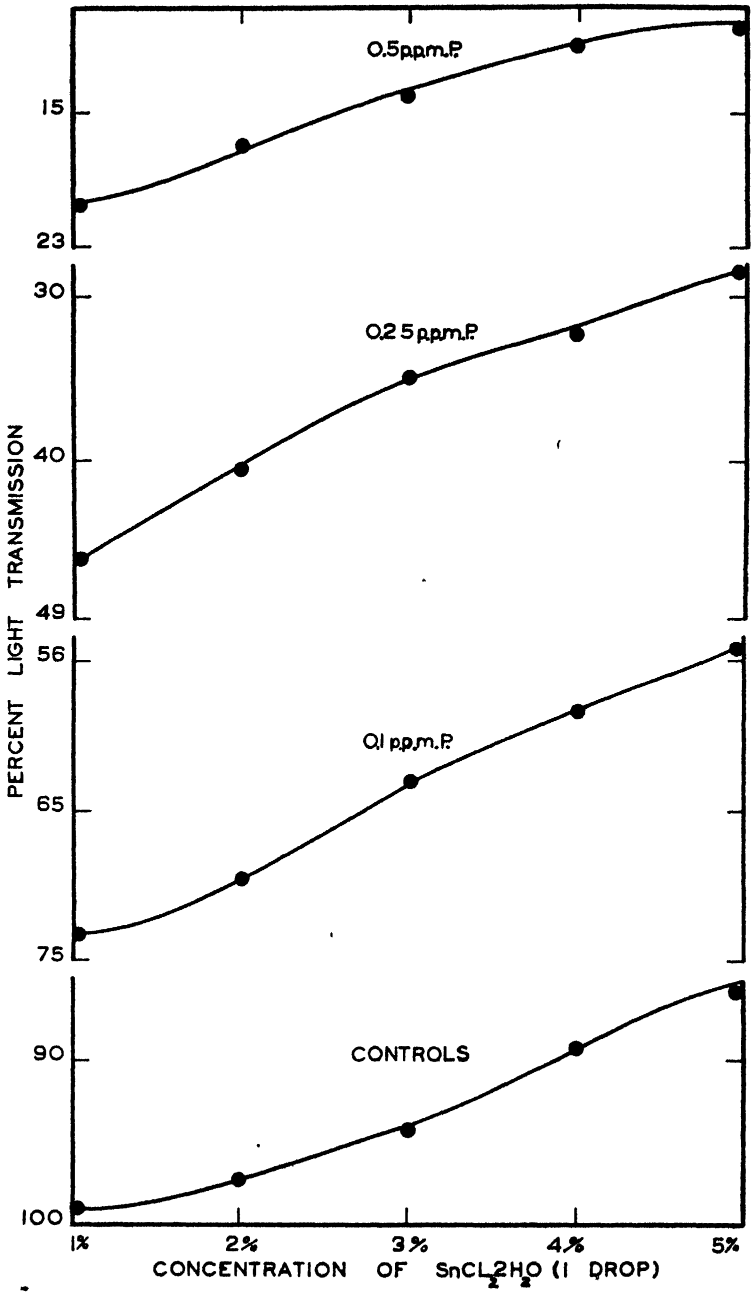

FIG. 2. *The effect of stannous chloride on the maximum colour intensity. (Temperature of all solutions, 23.5° C.)*

is stable. This influence of stannous chloride is due in part to the development of appreciable colour in the control solutions. The reaction involving phosphate is also affected since the K_1 values distinctly increase with increasing concentrations of stannous chloride even when correction is made for the control solution (see Table I).

TABLE I

EFFECT OF INCREASING AMOUNTS OF STANNOUS CHLORIDE ON THE CALIBRATION CONSTANT (TEMPERATURE OF ALL SOLUTIONS, 23.5° C.)

$SnCl_2 . 2H_2O$	Value of K_1		
	0.1 p.p.m. P	0.25 p.p.m. P	0.5 p.p.m. P
1 drop of 1% $SnCl_2 . 2H_2O$	1.35	1.33	1.34
1 drop of 2% $SnCl_2 . 2H_2O$	1 48	1 52	1.51
1 drop of 3% $SnCl_2 . 2H_2O$	1 74	1 72	1.65
1 drop of 4% $SnCl_2 . 2H_2O$	1.78	1.78	1.81
1 drop of 5% $SnCl_2 . 2H_2O$	1 94	1.94	1.88

Fig. 2, showing the effect of stannous chloride on the maximum colour intensity, is intended to supersede the same figure of the earlier paper (3), as it shows better the effects of different amounts of stannous chloride on colour development.

The data in Fig. 1 show quite different rates of colour development and fading than were previously observed [(3), Fig. 3]. With the new sample of stannous chloride the colour developed more slowly, and for a given amount of phosphorus was finally more intense and more stable than with the old sample, even when the comparison was made with equal additions of stannous ion. From this standpoint the main difference between the two reagents would be the greater proportion of stannic ion in the old preparation. According to Hein, Burawoy and Schwedler (4), stannic ion influences the reaction equilibrium.

An experiment was carried out to test the hypothesis that the difference in the action of the two samples of stannous chloride was due to their content of stannic ion. To aliquots of a phosphate solution were added varying amounts of a 2.5% solution of stannic chloride and the usual reagents. The results are shown in Fig. 3. Stannic ion causes the fading to take place sooner, and, in higher concentration, inhibits the maximum colour development. These results would then appear to explain why the two solutions of stannous chloride should result in different behaviour even when compared on the basis of equal concentrations of stannous ion. Probably no two samples of stannous chloride will give identical results. Consequently, whenever new stannous chloride reagent is employed it is necessary that a new calibration be made, and the time required for maximum colour development determined.

In the technique used, the galvanometer was adjusted to give a reading of 100, corresponding to maximum scale deflection, before addition of the stannous chloride, in order to compensate for any colour in the soil extract. Such a procedure is a satisfactory basis of comparison only if no blue colour develops in a phosphate-free solution. The results shown in Figs. 1 and 2 indicate that one drop of 1% stannous chloride reagent is about the maximum that can be added to each tube without the production of an appreciable colour in the control solution. This condition is satisfied if the stannous chloride solution is prepared in the following manner:— Dissolve 10 gm. of stannous chloride in 100 ml of 6*N* hydrochloric acid (redistilled) and dilute to 500 ml. with recently boiled distilled water. Titrate aliquots by the iodometric method of Scott (6) omitting the reduction of stannic ion, and calculate the true content of stannous chloride. Dilute to 1% with 1 2 *N* redistilled hydrochloric acid and store under hydrogen. If this is done the usual procedure of adding one drop of the reagent to each tube may be followed and the colour in the control solution will be small enough to ignore. However, larger amounts of stannous chloride may be used, provided that a correction is made for the colour developed in the control solution A typical calculation is given below. Suppose the galvanometer deflection for the control is 90. Then a reading of 50 for an unknown represents a percentage light transmission of $\frac{50 \times 100}{90}$.

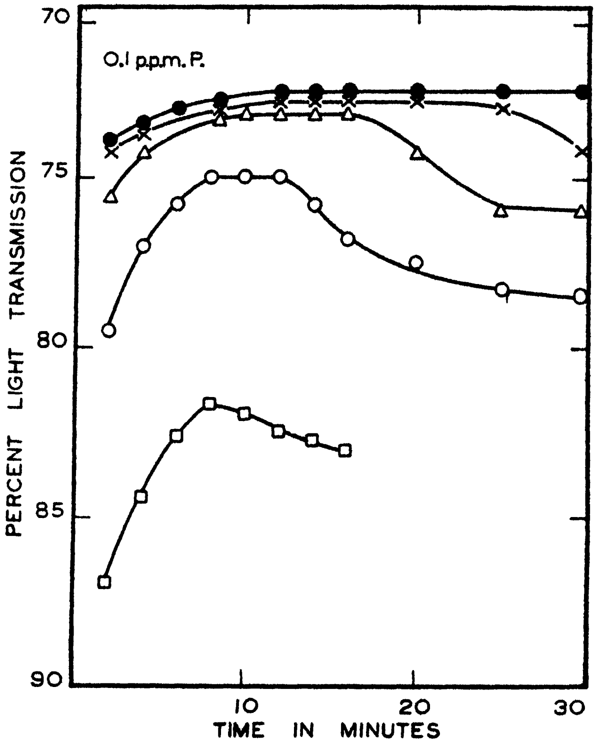

FIG. 3. *The influence of stannic ions on the colour development and fading.* ● *No* $SnCl_4$, × *1 drop of* $SnCl_4$, △ *3 drops of* $SnCl_4$, ○ *6 drops of* $SnCl_4$, □ *10 drops of* $SnCl_4$ *(Temperature of all solutions, 24° C, 21 drops equal 1 cc, 1 drop of 1%* $SnCl_2 \cdot 2H_2O$ *used in all solutions.)*

Deterioration of Stannous Chloride Reagent

In view of the effect of stannous and stannic ions on the colour development, the stability of the stannous chloride reagent is important. Oxidation will tend to lessen the stability of the colour, and to diminish the calibration constant.

Since stannous chloride, both in the solid form and in solution, is oxidized when exposed to the atmosphere, some precaution must be taken to minimize this change. The recommendation of Truog and Meyer (9) that the surface of the solution be covered with a layer of mineral oil to retard oxidation appears to have been generally adopted. However, even under oil a considerable deterioration goes on. It was observed that 10% of the stannous ion in a 1% solution of stannous chloride was oxidized in two weeks, even when protected in this manner.

The apparatus used by Sutton (7) to prevent the oxidation of titanous chloride proved to be very effective for the preservation of the stannous chloride reagent. The method consists in storing the solution under hydrogen, supplied by a small automatic generator which is connected in a closed system with the stannous chloride bottle. No deterioration of the reagent could be detected after more than a month of storage under hydrogen.

Effect of Chloride

It is well known that the common inorganic anions, when present in sufficient amounts, affect the course of the ceruleomolybdate reaction. According to Chapman (2) sulphates intensify the colour, nitrates have little or no effect on the colour maximum but induce an earlier, more pronounced fading, while chlorides reduce the colour maximum and cause earlier fading.

The action of chloride was studied because it was of interest in connection with a method for determining organic phosphorus, details of which will appear elsewhere in this Journal. Some of the data on this effect are shown in Fig. 4. The action of ammonium chloride in decreasing the colour development and causing early fading is evident. Further, it has been observed that the effect of sodium chloride is almost identical with that of ammonium chloride, so the action seems to be entirely due to the chloride ion.

These results illustrate the magnitude of the errors that may occur through overlooking the action of dissolved salts. For accurate visual colorimetry, it is necessary that the standard be made to contain an equal concentration of the salts that are present in the unknown with which it is to be compared. Similarly, in the photoelectric method, the calibration constant that is applicable to an unknown solution must be determined from the colour intensity developed in a standard phosphate solution containing equal concentrations of the ions that affect the reading.

The results obtained here indicate that the calibration constant is affected to about the same extent at different phosphate levels by a given, moderate salt concentration. In the ordinary instance, where a known amount of chloride or sulphate has been produced in a solution by neutralization, it is a simple matter to obtain a valid calibration constant, and so avoid appreciable errors. If, however, the chloride concentration is so great as to cause early fading it is rather difficult to obtain accurate results.

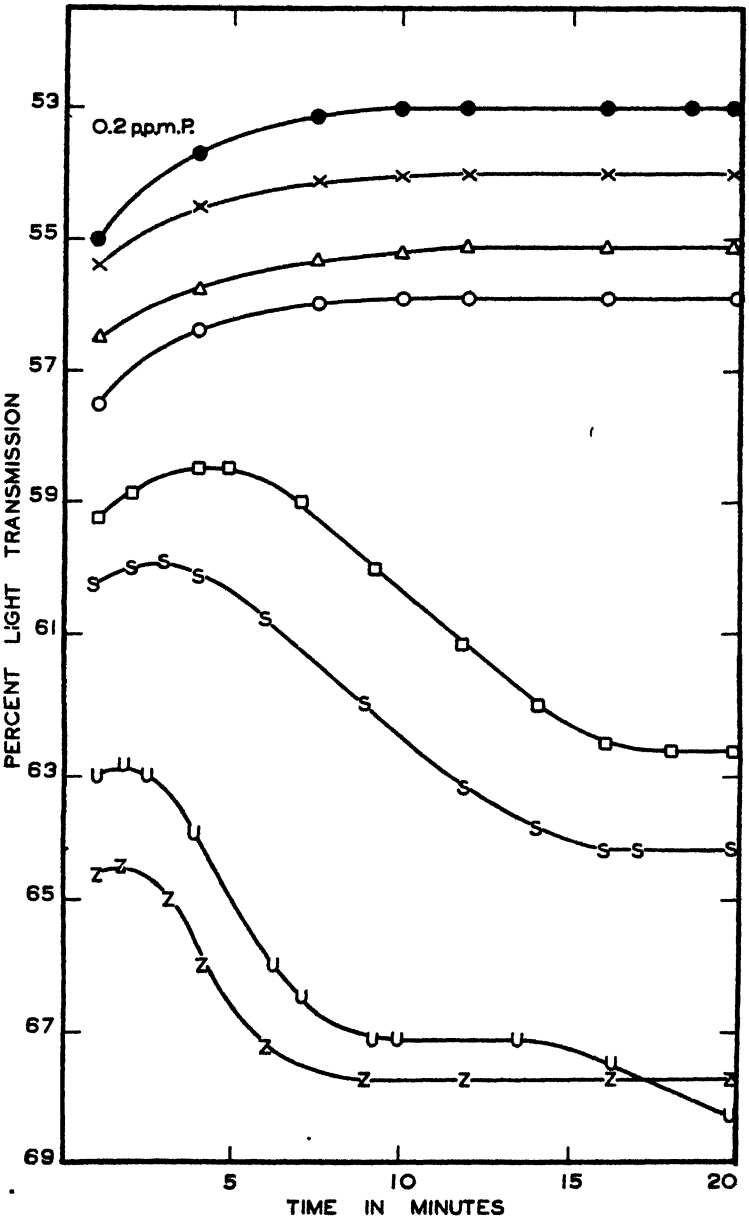

FIG. 4. *The effect of chloride concentration on colour intensity and fading.* ● *No chloride ion.* × *700 p.p.m. chloride ion;* △ *1400 p.p.m. chloride ion;* ○ *3500 p.p.m. chloride ion;* □ *9300 p.p.m. chloride ion;* S *18,600 p.p.m. chloride ion;* U *37,200 p.p.m. chloride ion;* Z *46,500 p.p.m. chloride ion. (Temperature of all solutions, 21° C.)*

Effect of Temperature

Occasionally, but particularly during the spring and summer months, seemingly unaccountable variations of the calibration constant have been observed. A study of the conditions associated with these aberrations led to the belief that temperature fluctuations might be responsible for the trouble.

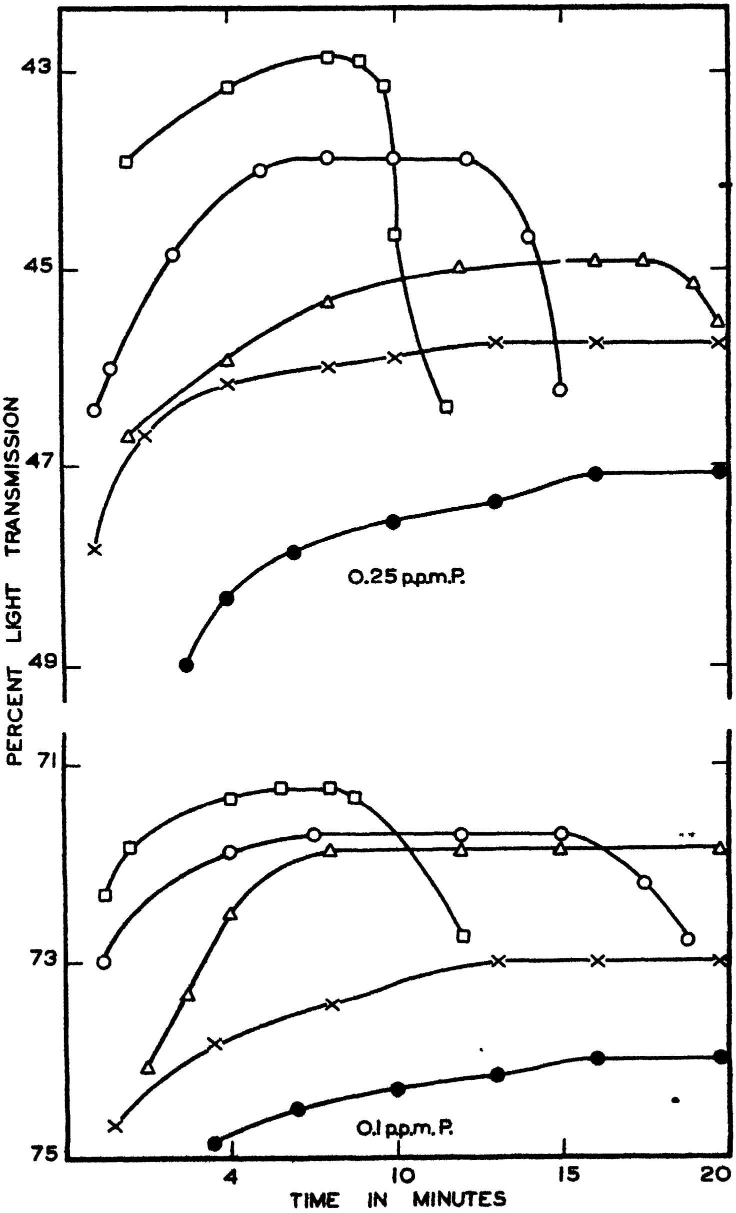

FIG. 5. *The influence of temperature on the development and stability of the colour.* ● *15° C.;* × *20° C.;* △ *24° C.;* ○ *28° C.;* □ *35° C. (1 drop of 1%* $SnCl_2 . 2H_2O$ *used to develop colour in all solutions.)*

As was noted previously (3), temperature exerts an effect on the intensity of the blue colour. More definite information on the nature and extent of this effect was sought. Fig. 5 shows curves obtained by following the colour development in two different phosphate solutions at several temperatures that cover the range of probable working conditions. The colorimeter tubes were placed in small water baths adjusted to the desired temperatures throughout the course of the reaction, and removed at intervals for the short time required to take a reading. Although the temperature might have changed slightly during the time when the readings were made, the results show clearly enough that the prevailing temperature exerts a significant effect on the colour development, and hence calibration data are strictly valid only for the temperature at which they were obtained. An increase in temperature results in an increase in the maximum colour development, and also in the reaction rate, as indicated by more rapid colour development, and decreased stability. The results indicate that it would be desirable to carry out the determinations under constant temperature conditions. Failing this, it has proved quite satisfactory in practice to include a standard phosphate solution in each set of determinations, and thus to establish the appropriate K_1 value to use with that set.

Table II records the values of K_1 corresponding to the maximum colour development at each temperature studied. It is clear that the effect of temperature on the calibration constant is the same at both phosphate levels.

TABLE II

THE EFFECT OF TEMPERATURE ON THE CALIBRATION CONSTANT

Temperature, °C.	Value of K_1	
	0.1 p.p.m. of P	0.25 p.p.m. of P
15	1.31	1.30
20	1.37	1.35
22	1.43	1.39
24	1.43	1.39
26	1.44	1.43
28	1.44	1.43
30	1.46	1.47
35	1.47	1.48

Effect of Ferric Iron

In the course of some recent determinations of the phosphorus content of soil colloids, it was observed that much higher values of phosphorus were obtained for diluted portions than for the original extract. Similar behaviour was attributed by Holman and Pollard (5) to an interference caused by dissolved organic matter. However, in the present instance it is certain that the effect was not due to organic matter, as ignition did not eliminate the interference.

The colour development and fading were studied in soil extracts that showed this behaviour. Typical results are shown in Fig. 6. It is evident that in the more concentrated solutions the colour develops rapidly and fades almost

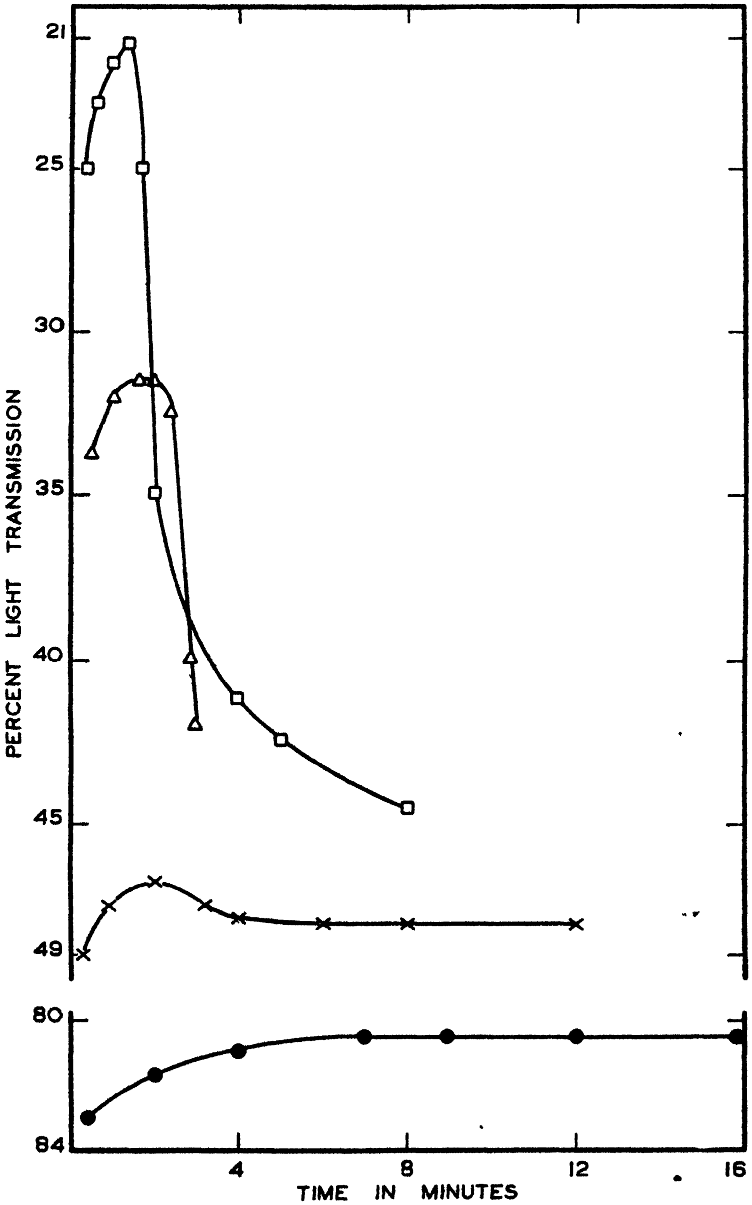

FIG. 6. *The nature of the interference due to iron observed in soil extracts.* ● *Acid extract before ignition. Dilution 1 to 10,000. Diluted extract contained 3 p.p.m. iron and 0.07 p.p.m. phosphorus.* × *Acid extract before ignition. Dilution, 1 to 2860. Diluted extract contained 10.5 p.p.m. iron and 0.24 p.p.m. phosphorus.* △ *Acid extract before ignition. Dilution, 1 to 2000. Diluted extract contained 15 p.p.m. iron and 0.34 p.p.m. phosphorus.* □ *Acid extract after ignition. Dilution, 1 to 2000. Diluted extract contained 15 p.p.m. iron and 0.54 p.p.m. phosphorus. (Temperature of all solutions, 24° C.)*

immediately, so that there is a sharp colour maximum within the first three minutes. Readings made five minutes after the addition of stannous chloride indicate much less than the maximum colour development. On dilution of the original solution in successive stages this sharp rise to a maximum is less apparent and is finally absent. The effect was observed to be the same in the ignited extracts as in those where organic matter was present.

Analyses showed that the solutions which exhibited this behaviour contained ferric iron in considerable concentrations. The interference of ferric iron was then studied in an attempt to account for the observed results. The colour development and fading were traced in phosphate solutions containing various known concentrations of ferric iron. The data obtained are reproduced graphically in Fig. 7. At the phosphorus concentration used in this experiment, 0.2 p.p.m., the effect of 1.0 p.p.m. of iron is negligible, but all

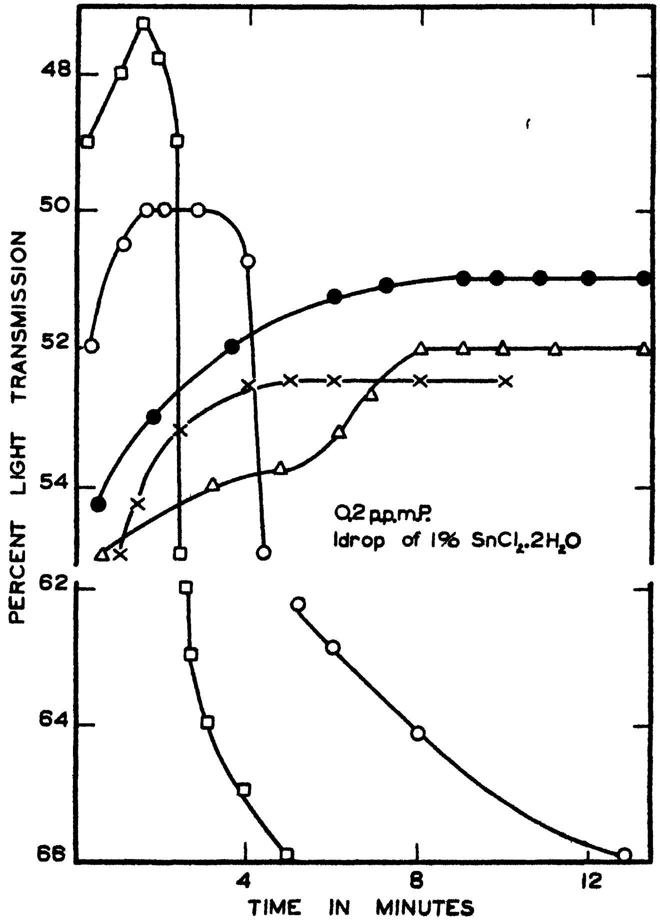

FIG. 7. *The influence of ferric iron concentration on the behaviour of the colour, using one drop of 1% stannous chloride reagent.* ● *No ferric iron;* × *5 p.p.m. of ferric iron;* △ *10 p.p.m. of ferric iron;* ○ *20 p.p.m. of ferric iron;* □ *35 p.p.m. of ferric iron. (21 drops equal 1 cc.; temperature of all solutions, 24° C.)*

the higher concentrations of iron cause appreciable errors. Thus, 2, 5, and 10 p.p.m. of iron prevent the normal colour development, whereas 20 and 35 p.p.m. of iron result in a rapid rise to an abnormal maximum, followed by early and rapid fading. It has also been observed that when the phosphorus con-

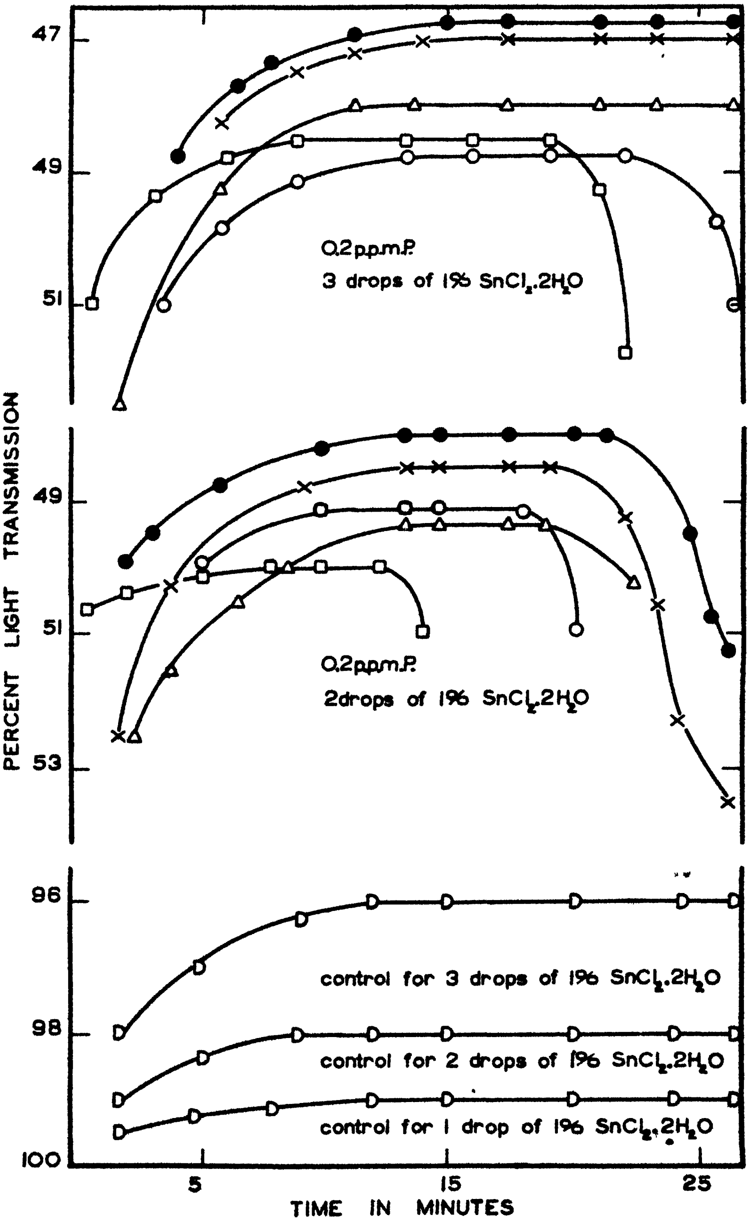

FIG. 8. *The influence of the ferric iron concentration on the behaviour of the colour, using two and three drops of 1% stannous chloride.* ● *No ferric iron;* × *5 p.p.m. ferric iron;* △ *10 p.p.m. ferric iron;* ○ *20 p.p.m. ferric iron;* □ *35 p.p.m. ferric iron. (Temperature of all solutions, 24° C.; 21 drops equal 1 cc.)*

centration is higher, less iron is required to cause interference. For example, with a phosphorus concentration of 0.5 p.p.m., 10 p.p.m. of iron causes an abnormal maximum and rapid fading. In many instances it has been found possible to dilute extracts until the interference due to iron was no longer appreciable.

Since ferric iron will rapidly oxidize stannous tin to the stannic condition, it was thought that the iron interference might be due, in part at least, to this action. As has been shown, the concentrations of both stannous and stannic ions exert important influences on the colour development. Accordingly, the above experiment was repeated, two and three drops of stannous chloride reagent being added instead of the usual one drop. The results are given in Fig. 8. The iron interference is considerably decreased by using larger amounts of stannous chloride. Abnormal maxima do not occur even with 35 p.p.m. of iron, and the deviation from the normal curve is less at all the iron concentrations.

Various attempts were made to overcome the interference of ferric iron by adding reducing agents other than stannous chloride to the solutions. It was found, however, that these additional substances themselves had specific effects on the colour development, and hence served only to complicate further the interpretation of results. Also, the interference due to ferrous iron is technically a difficult one to avoid. The use of potassium cyanide, as recommended by Tischer (8), was found to be ineffective.

The interference due to ferric iron probably can be circumvented best by diluting the extract as much as the phosphorus content will permit (to 0.1 p.p.m. of phosphorus is a suitable dilution), and, if the iron interference is still appreciable, by using two or three drops of stannous chloride, instead of one drop. However, as already pointed out, the addition of larger quantities of stannous chloride will necessitate a correction for the colour development in the control solution.

Discussion

The nature of the so-called ceruleomolybdate reaction of phosphate ions is not thoroughly understood. The reduction of a variety of molybdate complexes to form blue-coloured products will proceed without the intervention of phosphate provided that the acidity of the medium is not too great. Berenblum and Chain (1) contend that the role of phosphate is that of a catalyst which promotes the reduction and is itself inactivated in the process, and there is good experimental evidence in support of this view.

The colorimetric behaviour is rather characteristic. The colour develops to a maximum, remains constant for a time, then fades quite rapidly, and finally very slowly. Substances which influence the reaction affect both the intensity and the stability of the blue colour, but the phases of development, stability, rapid fading, and subsequent stability are always apparent. No simple explanation of this typical sequence can be offered.

The behaviour of the colour is such that the reaction is not easily applied quantitatively. In the use of the photoelectric technique, precautions must be taken to ensure that the calibration data are fully applicable to the solutions under test. The appreciable influence of temperature makes it necessary to establish the calibration constant that is currently valid each time readings are made. Calibration data obtained with pure phosphate solutions will not apply to solutions containing salts in appreciable concentrations. The appropriate calibration constant for such a solution must be obtained from the reading given by a standard phosphate solution containing the salts in identical concentrations.

The appropriate time for reading the colour maximum may not be generally prescribed, because of the probable differences between individually prepared stannous chloride reagents, and because colour stability decreases with increasing phosphate concentration. Each worker should determine the interval for taking readings that is appropriate under his own conditions. Gradual deterioration of the stannous chloride reagent may be avoided by storing it under an atmosphere of hydrogen.

The interference due to ferric iron is largely attributable to oxidation of the stannous ion. In all the practical instances so far encountered, the interference may be overcome by dilution and the use of excess stannous chloride reagent.

The ceruleomolybdate reaction of phosphates is extremely sensitive. The concentration of phosphorus in the final dilution should never exceed 0.5 p.p.m. and should preferably be about 0.25 p.p.m. Even minute amounts of perspiration and saliva contain enough phosphate to produce considerable errors. Consequently it is necessary to be unusually vigilant against contamination of the final solutions.

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s-DIPHENYLGUANIDINE AS AN ACIDMETRIC STANDARD[1]

BY J. W. YOUNG[2]

Abstract

s-Diphenylguanidine may be purified by recrystallization to provide a satisfactory acidmetric standard. The results of titration of an alcoholic solution of the base to pH 5.2 for N acid or 5.6 for $N/10$ acid agree within experimental error with values obtained with sodium carbonate or borax. Three methods of preparing borax containing exactly 10 molecules of water of crystallization have been compared, *viz.*, drying over sodium bromide, drying over a saturated solution of sugar and salt, and washing with alcohol and ether. Satisfactory products resulted, but they were found to be unstable on storage. Sodium bicarbonate has been found to be stable on long storage. The density of *s*-diphenylguanidine at 20° C. was found to be 1.19.

The commonly used standards for alkaline solutions are in general satisfactory, and may be said to meet the specifications proposed by various writers (2; 7, p. 39; 10). The substances most generally used are potassium acid phthalate and benzoic acid. The recent addition of furoic acid (6) has provided at least three substances that are easily purified, are stable in air, and contain no water of crystallization.

Unfortunately there are no completely satisfactory acidmetric standards, and most commercial laboratories prefer to standardize acid solutions by the use of a standard alkali that has been checked by one or more of the alkalimetric standards mentioned. The two acidmetric standards most commonly used are sodium carbonate and borax. Sodium carbonate is very hygroscopic, must be freshly prepared from sodium bicarbonate or sodium oxalate, and may be weighed only by the application of special precautions (8). Borax containing exactly 10 molecules of water may be prepared by a time-consuming process (8, 9), or by the use of special solvents (5). It is not stable with respect to water content on storage or on exposure to air (5).

The use of *s*-diphenylguanidine was originally proposed by Carlton in a preliminary study (1), but it has not been critically investigated. A recent publication (11) records a preliminary study of this material and mentions difficulty in the application of Carlton's method of purification.

Sodium bicarbonate has not been thoroughly investigated but appears to have the merit of being stable in air (9).

Other standard substances, notably potassium iodate, calcite, and mercuric oxide, have, owing to low equivalent weight, limited application, or difficulty of purification, not received wide acceptance.

In this study the writer attempted to devise a suitable method for the purification of *s*-diphenylguanidine, and to compare this standard with the commonly accepted standards, sodium carbonate and borax. The various methods of purification of borax were compared, and some observations were made on the stability of sodium bicarbonate.

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[1] *Original manuscript received October 11, 1938.*
Contribution from the Laboratory, Glenmore Water Supply, City of Calgary, Alberta, Canada.

[2] *Chemist, Laboratory, Glenmore Water Supply, Calgary.*

Apparatus

In all titrations a special burette was used.* This instrument was built of Pyrex glass and consisted of a bulb of 49 ml. capacity attached to a graduated tube divided in 0.01 ml. from 49 to 55 ml. A series of special temperature correction tables were prepared, and the instrument was standardized for various drainage times. On the basis of these standardizations it was found that the probable error of determination of a delivered volume varied from 0.002 to 0.004 ml., the actual error depending on the amount delivered, the lower reading applying to volumes from 49 to 51 ml.

In use, the burette was adjusted to zero after the temperature of the contents had been read, and the acid solution was allowed to flow into the solution of base to be titrated with the cock full open until the volume of solution added was within 0.1 ml. of the end-point, as established by a preliminary titration. The titration was then carefully completed, and a series of volume readings taken at intervals of 5, 6, 7, 10, 15, and 20 min. from the start of the titration. Standardization curves using these drainage times were applied and temperature corrections made. No differences could be detected between the drainage of normal hydrochloric acid solution and that of water, although the temperature corrections were of course very different.

In titrations of carbonate solutions the last 0.1 to 0.2 ml. of acid was added from a micro burette after successive boilings to remove carbon dioxide.

All titrations were made in Pyrex flasks, solvents being of the highest purity obtainable. Blank titrations showed insignificant quantities of base in the alcohols used as solvents for *s*-diphenylguanidine. Standardized weights were used, and all weighings were corrected to vacuum.

Preparation of Materials

Sodium Carbonate. A sample of very pure sodium bicarbonate, free from chloride, sulphate, and potassium, was used as the source of sodium carbonate. This material was converted to sodium carbonate by heating in small crucibles to constant weight at 180° to 300° C. These tests showed that sodium bicarbonate itself is very stable in air. In using this supply, as stored in the stock bottle, the data in Table I were obtained.

Suitable quantities of sodium bicarbonate were weighed into crucibles, heated to constant weight, and the sodium carbonate was transferred to titra-

TABLE I

RESIDUES ON HEATING SODIUM BICARBONATE

Date	Aug. 12, 1935	Nov. 30, 1935	May 23, 1936	June 11, 1937
Residue at 280° to 300° C., %	63.143	63.148	63.144	63.147

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* *This burette was built to the writer's specifications by the Scientific Glass Apparatus Company, Bloomfield, N.J.*

tion flasks with a stream of hot water. The volume was made up to 50 ml. and acid added to within 0.1 ml. of the expected end-point. The solution was boiled, cooled, and titrated to the end-point using the selected indicator and a buffer mixture as standard. The procedure of boiling and cooling was repeated until no further acid was required. Two such treatments were usually sufficient. The titration error using methyl orange and titrating to pH 4.0 was found to be 0.014 ml. of *N* hydrochloric acid for a volume of 100 ml. The titration error using brom cresol purple was not appreciable.

Borax. Three samples of borax were prepared, all from a specially purified grade.

Borax A. This borax was twice recrystallized from water and dried for eight months over sodium bromide. It was stored in a stoppered bottle until used.

Borax B. This material was recrystallized in the same manner as Borax A, but was stored for eight months over a solution saturated with respect to both sucrose and salt. It was stored as was preparation A (9).

Borax C. This borax was recrystallized once from water, the wet crystals were sucked as dry as possible on a Büchner funnel, and washed three times with 92% ethyl alcohol and three times with ether. It was dried for 30 min. in air, and bottled (5).

The data in Table II were obtained on ignition of these preparations.

TABLE II

RESIDUES ON HEATING BORAX

Preparation	*A*	*B*	*C*	Theory
Residue on ignition, %				
September, 1937	52.765	52.790	52.796	52.769
October, 1937	52.819	52.844	52 819	

It will be noted that these preparations lost water over a period of one month, during which they were opened for use in standardizations. These results confirm those of Hurley (5) and indicate the instability of borax on ordinary storage.

Since the standardizations were performed at times between those of the two series of determinations given in Table II, the mean values of these residues on ignition were used in calculation of standardizations.

It was also noted that storage of borax in a warm place (40° C.) resulted in loss of water of crystallization, which condensed in the upper part of the bottle. Storage for one hour caused a loss of 0.64% in weight of 150 gm. of salt.

The procedure in standardization was to dissolve the weighed borax in water (50 ml. in the case of 0.1 *N* acid and 100 ml. with *N* acid), add the appropriate indicator, and titrate until a match was obtained with a solution prepared from sodium chloride and boric acid and diluted to the expected final volume of titration.

s-Diphenylguanidine. The several methods used for purification had been tried on various batches of material in preliminary experiments, and had given satisfactory results in standardizations. Quantities used were weighed to give final products weighing 100 to 200 gm. Solvents were recovered by distillation and used several times. Solutions were kept in Pyrex glass or porcelain, but were not protected from carbon dioxide in the air. All products were dried at 90° to 100° C. and stored in stoppered bottles until used. Repeated analyses showed less than 0.02% moisture absorption on long storage.

s-Diphenylguanidine A. Eastman Kodak Co. product. Ash, 0.01%; m.p., 148.2° C.(d).

s-Diphenylguanidine B. Material A, twice recrystallized from toluene. Yield, 81%; ash, 0.01%; m.p., 148.5° C.(d).

s-Diphenylguanidine C. The base was dissolved in a minimum quantity of methanol, precipitated by dilution with water, filtered, and dried. The dried material was recrystallized three times from toluene. Yield, 73%; ash, 0.005%; m.p., 148.9° C.(d).

s-Diphenylguanidine D. The residues from a series of titrations (the chloride salt of the base) were combined, precipitated with excess sodium hydroxide solution, and washed with hot water until free from chlorides. The base was dried and recrystallized three times from toluene. Yield, 66%; ash, 0.015%; m.p., 148.9° C.(d).

s-Diphenylguanidine E. The original material was washed with toluene, recrystallized once from toluene, dried, precipitated from methanol and water as with preparation C, dried, and recrystallized five times from toluene. Yield, 53%; ash, 0.01%; m.p., 149.0° C.(d).

In all cases, decomposition occurred above 100° C., as is noted in the melting point determinations. Some decomposition may occur at lower temperatures, so a minimum time of drying was adopted in all cases.

The density of *s*-diphenylguanidine is not recorded in the literature, and a value was required for use in the reduction of weighings to *vacuo.* Two determinations using heptane saturated with the base as displacing liquid gave values of 1.187 and 1.186 at 20° C. Determinations in a gas volumeter of the type described by Francis and Oxnard (3) gave values of 1.16 and 1.18. The value accepted for this work was 1.19.

The method used in these titrations consisted in dissolving the weighed base in 40 ml. of the solvent selected using gentle heat, and titrating to the end-point with the acid.

The end-points used in this work differ from those adopted by previous investigators (1, 11). Selected values were based on determinations of dissociation constants given by Hall and Sprinkle (4). On the basis of their results, in approximately 40% alcohol solutions, the end-points selected were pH = 5.2 for the titration of *N* acid and pH = 5.6 for *N*/10 acid. In all cases the end-points were very sharp, being detectable to 0.005 ml. of 0.1 *N* acid. A buffer mixture was prepared to contain the appropriate indicator at the proper pH. In the case of methyl red the colours of alcoholic and aqueous solutions cannot be matched exactly, but the error was not significant.

Standardizations

The results of standardizations are presented in Table III.

TABLE III

ACID STANDARDIZATIONS

Standard substance	Solvent	Indicator*	Factors	Mean factor
N Hydrochloric acid				
Na_2CO_3	H_2O	M.O.	0.9959, 0.9957, 0.9953, 0.9951	0.9955
Na_2CO_3	H_2O	B.C.P.	0.9951, 0.9950, 0.9951, 0.9951	0.9951
$Na_2B_4O_7$A	H_2O	M.O.	0.9951, 0.9954, 0.9950, 0.9957, 0.9958	0.9954
$Na_2B_4O_7$B	H_2O	M.O.	0.9949, 0.9949, 0.9950, 0.9951	0.9950
$Na_2B_4O_7$C	H_2O	M.O.	0.9960, 0.9954, 0.9956, 0.9956, 0.9956	0.9956
$C_{13}H_{13}N_3$A	C_2H_5OH	M.R.	0.9959, 0.9962, 0.9962	0.9961
$C_{13}H_{13}N_3$B	C_2H_5OH	M.R.	0.9959, 0.9959, 0.9956	0.9958
$C_{13}H_{13}N_3$C	C_2H_5OH	M.R.	0.9953, 0.9954, 0.9955	0.9954
$C_{13}H_{13}N_3$D	C_2H_5OH	M.R.	0.9959, 0.9957, 0.9957	0.9958
$C_{13}H_{13}N_3$E	C_2H_5OH	M.R.	0.9956, 0.9957, 0.9955, 0.9957	0.9956
$C_{13}H_{13}N_3$E	CH_3OH	M.R.	0.9954, 0.9956	0.9955
$C_{13}H_{13}N_3$E	CH_3OH	B.C.G.	0.9957, 0.9957	0.9957
$C_{13}H_{13}N_3$E	*iso*-C_3H_8OH	M.R.	0.9958, 0.9959, 0.9957	0.9958
N/10 Hydrochloric acid				
Na_2CO_3	H_2O	M.O.	0.9819, 0.9817, 0.9819, 0.9824, 0.9823	0.9820
$Na_2B_4O_7$A	H_2O	M.R.	0.9819, 0.9824, 0.9819, 0.9826, 0.9824	0.9822
$C_{13}H_{13}N_3$B	C_2H_5OH	M.R.	0.9823, 0.9825, 0.9825, 0.9826	0.9825
$C_{13}H_{13}N_3$E	C_2H_5OH	M.R.	0.9824, 0.9820, 0.9826	0.9823

* *Indicators*—M.O., *methyl orange*, M.R., *methyl red*, B.C.P., *brom cresol purple*, B.C.G., *brom cresol green.*

In general, properly purified *s*-diphenylguanidine is a satisfactory acidimetric standard, giving results agreeing within 0.05% of those obtained with borax or sodium carbonate. Methyl, ethyl, and isopropyl alcohols are satisfactory solvents for the base to be titrated, methyl red and brom cresol green being suitable indicators for the titration exponents selected. The chloride salts obtained on titration may be used as a source of the free base which may be purified and used again. The commercially available purified material gives results within 0.1% of those obtained with the purified base. The base is stable on long storage, attracting at most 0.02% of moisture.

Three methods of so preparing borax as to contain exactly 10 molecules of water of crystallization have been compared. All methods tend to give a product that is slightly low in water, and the material is not stable on ordinary storage.

It was noted that sodium bicarbonate shows stability on long storage, the composition remaining constant to 0.01% or better. The presence of carbon dioxide renders accurate titration difficult.

Acknowledgment

The writer wishes to express his appreciation to Mr. W. E. Robinson, waterworks engineer, City of Calgary, for his interest in this work, and for permission to publish this paper.

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A METHOD FOR THE DETERMINATION OF ORGANIC PHOSPHORUS IN SOILS AND SOIL EXTRACTS[1]

BY C. L. WRENSHALL[2] AND W. J. DYER[3]

Abstract

Dissolved organic phosphorus may be determined, even in highly coloured alkaline soil extracts, by the application of photoelectric colorimetry to the ceruleomolybdate colour reaction of phosphate ions. Total organic phosphorus may be extracted from soil with 4 *N* hydrochloric acid followed by treatment of the residue with 3 *N* ammonium hydroxide. Inorganic phosphorus is determined by direct colorimetry in the acid extract and in the acidified alkaline extract. Total phosphorus is determined similarly in each extract after ignition. The difference between total and inorganic phosphorus is equivalent to the organically combined phosphorus content of the soil sample.

The soil organic phosphorus was found to be stable under these treatments. A considerable proportion of the organic phosphorus is extracted by acid, and the total soil phosphorus is almost completely extracted by the two treatments with 4 *N* hydrochloric acid and 3 *N* ammonium hydroxide.

Introduction

One of the recent trends in soil chemistry is to resume the study of the soil phosphorus that is combined in organic compounds. This subject is being approached with two objectives; first, to obtain a better knowledge of the chemical combinations in which the soil phosphorus exists, and second, to explain the role of organic phosphorus in the complex cycle of phosphate in the soil. A review of the literature shows that no completely satisfactory method for the determination of organic phosphorus in soils and soil extracts has been proposed.

Parker and Fudge (6) applied the ceruleomolybdate colour reaction of phosphate ions to the determination of organic phosphorus in water extracts of soils. Inorganic phosphate was determined directly in an aliquot, and total phosphorus in another aliquot after ignition. The difference was taken to be organic phosphorus. This method was very limited in its application, since for visual colorimetry it was necessary to have colourless solutions.

Recently Dean (2) employed the same principle in determining organic phosphorus in alkaline soil extracts which he decolorized with kieselguhr or by treatment with bromine. Experiments in this laboratory indicate that complete decolorization is not attained by the action of bromine, and

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that the treatment with alkali and bromine is sufficiently drastic to release some phosphorus from organic combination.

Various methods have been proposed for determining total soil organic phosphorus by using the ceruleomolybdate reaction in conjunction with treatments designed to release phosphate from its organic linkage. Odynsky (5) determined the increase in acid soluble phosphate produced by igniting the sample. Recently Dickman and De Turk (3) published the details of a method based on releasing the organic phosphorus by treatment with hydrogen peroxide. In both these methods the whole soil is subjected to the destructive treatment and there is a danger that released phosphate may become fixed by the soil residue. Davis (1) has demonstrated that some soils may absorb phosphate from a medium with a pH value as low as 0 25. The usefulness of these methods is limited because they may not be applied to coloured solutions, such as alkaline soil extracts, where direct visual colorimetry is impracticable.

In a previous paper (4) the authors showed that it is possible to differentiate between organic and inorganic phosphorus in various soil extracts, including those containing coloured organic matter, by the use of a photoelectric colorimeter. It was thought that if all the organic phosphorus of soil could be brought into solution by suitable means, a determination of the total organic phosphorus could be effected. Such an approach proved feasible, and resulted in the method described herein. The method has been used with practical success since September, 1937.

Procedure

A. Extraction

A 1 gm. sample of finely ground soil (100 mesh) is placed in a 50 ml. Erlenmeyer flask and treated with 25 ml. of 4 *N* hydrochloric acid (redistilled). The contents are mixed by gentle rotation several times during the first hour, and then allowed to stand overnight. The mixture is filtered through hardened filter paper, and the residue washed with hot 0.01 *N* hydrochloric acid, it being completely transferred to the filter in the process. Washing with pure water sometimes causes peptization of organic matter. The filtrate is collected in a 100 ml. volumetric flask, cooled, and diluted to volume.

The residue from the acid extraction is then washed into a 100 ml. volumetric flask containing 20 ml. of concentrated ammonium hydroxide, and diluted to volume. The flask is stoppered and the contents are mixed several times during an hour, and allowed to stand until the following day. A quantity of this extract is centrifuged at moderate speed (3000 r.p.m.) for a few minutes to remove suspended material before aliquots are withdrawn for analysis.

B. Preparation for Total Phosphorus Determination

A 10 ml. aliquot of the extract is placed in a silica evaporating dish containing 10 ml. of 1 *N* magnesium nitrate solution, and evaporated to dryness. Organic matter is completely destroyed by ignition at 550° C. After the dish has cooled sufficiently, 10 ml. of 1 *N* hydrochloric acid is added, and the covered dish is placed on the steam bath for two hours to bring about complete hydrolysis to orthophosphate. The contents of the dish are then washed into a 100 ml. volumetric flask and one drop of paranitrophenol indicator (0.5% solution in water) is added. The pH of the solution is adjusted to approximately 3.0 by adding dropwise 1 *N* ammonium hydroxide until the appearance of a yellow colour, then discharging the yellow colour with a drop of 1 *N* hydrochloric acid. The solution is diluted to volume. A suitable aliquot, usually 25 ml., is transferred to a 50 ml. volumetric flask, and 2 ml. of the Truog and Meyer (10) acid molybdate reagent is added; this final solution is diluted to volume, and is then ready for the colorimetric determination.

C. *Preparation for Inorganic Phosphorus Determination*

(1) On the acid extract. A small aliquot, usually 5 ml., of the acid extract, is pipetted into a 50 ml. volumetric flask, diluted to 30 to 40 ml., the pH adjusted to approximately 3 0, and finally diluted to volume after the addition of 2 ml. of acid molybdate reagent, as described above.

(2) On the alkaline extract. A 10 ml. aliquot of the centrifuged extract is acidified by the dropwise addition of 4 *N* hydrochloric acid with continuous stirring. Acidification is complete when the flocculent precipitate of "humic acid" forms. The mixture is filtered into a 50 ml. volumetric flask, and the precipitate is washed with 0.01 *N* hydrochloric acid until the volume of filtrate is about 40 ml. The filtrate is adjusted to pH 3.0, and diluted to volume after the addition of 2 ml. of acid molybdate reagent.

D. *Colorimetric Procedure*

The photoelectric colorimetry of phosphorus in soil extracts has been discussed at length elsewhere (4, 9), and only an outline of the necessary manipulations is given here.

A 10 ml. aliquot of the final solution, containing acid molybdate reagent, is pipetted into a colorimeter tube. The tube is placed in the colorimeter, in which the 660 mμ filter has been inserted, and the rheostat so adjusted that the galvanometer shows a reading of 100*. One drop of 1% stannous chloride reagent is then added and mixed with the contents of the tube, and the galvanometer reading is recorded when the colour has developed to a maximum, which is usually about 10 min. after the addition of stannous chloride. The minimum galvanometer reading, corresponding to maximum colour, gives directly the concentration of phosphate phosphorus at the final dilution, by reference to calibration data. The appropriate calibration constant is obtained by measuring the light absorption in a phosphate solution of known concentration which contains the same concentration of ammonium chloride as the unknown.

The results in this paper are expressed as milligrams of phosphorus per gram of soil.

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* *In reading a series of tubes it is convenient at this point to record the "centre setting", i.e., the galvanometer reading when the tube is removed. After the colours have been developed, adjustment to the appropriate centre setting is made for each tube before it is placed in the colorimeter for the final reading.*

Results and Discussion

Some results obtained by the use of the method are presented in Table I. It may be seen from these data that a considerable proportion of the organic phosphorus is brought into solution by the acid extraction. On the other hand, following the action of relatively strong acid, the ammonia solution dissolves only slight traces of inorganic phosphorus. The sum of the amounts of phosphorus dissolved by the two extractions approaches the total phosphorus of the soil, the percentage extraction being from 90 to 100% in the typical instances reported. The almost complete recovery of the phosphorus in the muck soils indicates that the extraction of organic phosphorus is complete. The agreement between duplicate values for the proportion of the soil phosphorus that is organically combined appears to be very satisfactory, when it is considered that these values may combine the errors of four colorimetric phosphorus determinations. The analysis of an ignited sample offers convincing proof that the method gives a true representation of the organic-inorganic phosphorus distribution.

Further extraction with ammonia of the residue from mineral soils brings no more phosphorus into solution. It may be assumed that the phosphorus not dissolved by the two extractions is inorganic phosphorus contained in undecomposed mineral fragments. In one case the phosphorus content of the grey, silicious residue from the extraction of a mineral soil was determined, after magnesium nitrate fusion, and proved to be about 6% of the total soil phosphorus. This result is in harmony with the data for percentage extraction.

In order to ensure that no interfering substances or conditions were affecting the direct determinations of inorganic phosphorus, known amounts of phosphate were added to some of the extracts, and the recovery of these known additions was noted. It was found that the recovery was 99 to 100% in the acid extracts, but rather less satisfactory in the alkaline extracts, ranging from 95 to 100%. It was thought that the "humic acid" precipitate might be adsorbing inorganic phosphate. Some of these precipitates were dissolved in dilute ammonium hydroxide, reprecipitated, and the phosphate in the filtrate was estimated. The merest traces of phosphate were found, and it was concluded that inorganic phosphate is not adsorbed to an appreciable extent. Inorganic phosphate was determined directly in a dilute solution of the alkaline extract in some instances where the dissolved organic matter did not give too flocculent a precipitate upon acidification of the solution. The results were almost identical with those given by the filtration method. The difficulty in obtaining complete recovery of the phosphate in the alkaline extracts appears to be due mainly to the high concentrations of ammonium chloride present in these solutions. As shown elsewhere, ammonium chloride in high concentration not only depresses the colour intensity but also renders the colour less stable, so that it is almost impossible to perform quantitative colorimetry. However, the amount of phosphate involved in this particular determination is such a small proportion of the total phosphorus that the effect upon the result of the method as a whole is negligible.

TABLE I

RESULTS OF ORGANIC PHOSPHORUS ANALYSES OF SEVERAL SOILS

Soil type	Soil No.	*	Milligrams of phosphorus per gram of soil									Per cent extraction	Org. P, % of total P
			Acid extract			Ammonia extract			Total P ext.	Total org. P	Total P of soil**		
			Total	Inorg.	Org .	Total	Inorg.	Org.					
Black muck	1	*a*	0.490	0.100	0.390	0.466	0.013	0 453	0.956	0.843	0.970	98.6	86.9
		b	0.490	0.099	0.391	0.455	0.017	0.438	0.945	0.829		97.4	85.5
	2	*a*	0.585	0.220	0.365	0.384	0.013	0.371	0.969	0.736	0.980	98.9	75.1
		b	0.612	0.220	0.392	0.380	0.008	0.372	0.992	0.764		101.2	78.0
Podsol	3	*a*	0.562	0.317	0.245	0.150	0.009	0.141	0.712	0.386	0.780	91.3	49.5
		b	0.562	0.317	0.245	0.150	0.009	0.141	0.712	0.386		91.3	49.5
	4	*a*	0.410	0.230	0.180	0.170	0.000	0.170	0.580	0.350	0.610	95.1	57.4
		b	0.400	0.220	0.180	0.168	0.002	0.166	0.568	0.346		93.1	56.7
Brown forest soil	5	*a*	0.530	0.370	0.160	0.176	0.012	0.164	0.706	0.324	0.789	89.5	41.1
		b	0.640	0.380	0.160	0.170	0.012	0.158	0.710	0.318		90.0	40.3
	6	*a*	1.150	0.910	0.240	0.210	0.022	0.190	1.360	0.430	1.350	100.8	31.8
		b	1.110	0.910	0.200	0 212	0.002	0.210	1.320	0.410		97.8	30.4
Ignited soil	7	*a*	0.837	0.837	0.000	0.040	0.037	0.003	0.877	0.003	0.900	97.4	0.3
		b	0.840	0.837	0.003	0.037	0.037	0.000	0.877	0.003		97.4	0.3

* *a and b represent duplicate extractions.*

** *Separate determinations of the total phosphorus were made colorimetrically after magnesium nitrate fusions of the soils.*

It is known that organic phosphorus compounds are fairly stable in both acid and alkaline solutions at ordinary temperatures (7), and Schollenberger (8) showed that dilute ammonium hydroxide does not have any destructive action on the organic phosphorus compounds in soil. It was nevertheless thought important to test the stability of soil organic phosphorus in the presence of the relatively strong acid used for extraction. A series of analyses of an acid extract showed no change in the phosphorus distribution in a period of 10 days. The acid concentration of the final extract is, however, only 1 *N*, and an experiment was designed to compare the effects of different concentrations of acid applied directly to the soil in the usual procedure.

Hydrochloric acid was used at the following concentrations: 0.5 *N*, 1 *N*, 3 *N*, 5 *N*. The results are summarized in Table II.

There does not appear to be any consistent difference between the results obtained with different concentrations of acid. The use of 4 *N* acid seems to be quite reasonable in the light of these data; in fact, it is evident that the concentrations of the extracting acid may vary between wide limits without affecting the determination. It is felt that this fact is in strong support of the validity of the present method.

Table II shows that the total phosphorus extracted is appreciably more when 3 *N* or 5 *N* acid is used. The solubility of organic phosphorus in the acid solution increases progressively with the concentration of acid, and ammonia extraction removes the remainder in each case. The amount of inorganic phosphate in the ammonia extract decreases as the concentration of the extracting acid is increased. This observation favours the extraction with strong acid (3 to 5 *N*) since its use minimizes the errors of colorimetry in regard to the alkaline extract. Indeed, when the acid used is 3 *N* or stronger, only a minor error would be incurred by assuming that all the phosphorus of the ammonia extract is organic phosphorus. This suggests a means by which a very good estimate of the organic phosphorus may be obtained without the use of a photoelectric colorimeter, as visual colorimetry is feasible in the acid extract.

TABLE II

INFLUENCE OF THE CONCENTRATION OF THE EXTRACTING ACID ON THE DETERMINATION OF TOTAL ORGANIC PHOSPHORUS

Concentration of extracting acid (HCl)	Milligrams of phosphorus per gram of soil*								Per cent ext'n	Org. P, % of total P
	Acid extract			Ammonia extract			Total P ext'd	Total org. P		
	Total	Inorg.	Org.	Total	Inorg.	Org.				
0.5 *N*	0.255	0.207	0.048	0.455	0.052	0.403	0.710	0.451	91.0	57.8
1 *N*	0.294	0.234	0.060	0.415	0.044	0.369	0.709	0.429	90.9	55.0
3 *N*	0.467	0.287	0.180	0.290	0.020	0.270	0.757	0.450	97.0	57.7
5 *N*	0.555	0.322	0.233	0.205	0.012	0.193	0.760	0.426	97.4	54.7

* *Soil No. 8—, a podsol, with a total P content (air dry) of 0.078%.*

The results in Table I suggest an interesting relation between soil type and the proportion of phosphorus organically combined. In muck soils, which owe their existence to the inhibition of organic decay, the proportion of organic phosphorus is very high. In the podsols, where the organic matter is poorly decomposed, the proportion of organic phosphorus is intermediate, and in the brown forest soils, where the decomposition of organic matter is well advanced, the proportion of organic phosphorus is lowest. It is, perhaps, of interest that soil No. 6 is a very fertile soil, probably the most fertile of the group analyzed. However, the data at hand are too few to permit any definite conclusions to be drawn in this connection.

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PRESSURE, VOLUME, TEMPERATURE RELATIONS OF ETHYLENE IN THE CRITICAL REGION. I.[1]

By J. Dacey[2], R. McIntosh[2], and O. Maass[3]

Abstract

Pressure isothermals of the system were determined both above and below the temperature of disappearance of the meniscus. Regions of constant pressure with changing volume were observed with all isothermals, in agreement with the prediction of Mayer and Harrison (2, 3). The complete envelope of this region above the critical temperature has not as yet been determined. The pressure of the heterogeneous system at 9 50° C. was found to correspond within experimental error to the pressure of the flat portion of the homogeneous isothermal at the same temperature. The pressure of this heterogeneous system was found to be independent of the mass-volume ratio; this is in agreement with the experimental behaviour previously discovered by the authors (5) for such a system at 9 80° C. Moreover, the pressure of the heterogeneous system was found to be identical with that of the system which had been heated at constant volume to a temperature at which the density difference in the tube is known to have been destroyed, and then cooled to the same temperature of 9 50° C.

The isothermal at 9 60° C. was studied, and shown to be the equilibrium curve at that temperature. A hysteresis was observed on reversing the direction of measurement, *i.e.*, from "vapour" to compressed "liquid". This hysteresis was found to be caused by the time lags which are observed in passing from the "vapour" region of an isothermal to regions of high density. Certain apparent discrepancies between the work of the present authors and that of Geddes and Maass have been observed and cannot as yet be explained.

The phenomena observed are interpreted on the basis of a difference between the gaseous and liquid states of aggregation, with a structure assigned to the latter.

Introduction

The present work is a continuation of that reported by McIntosh and Maass (5) on the density, pressure, and temperature relations of ethylene, and has been directed primarily toward the study of certain predictions made by Mayer and Harrison (2, 3) of the behaviour of condensing systems, and of the hypothesis of Maass that the liquid state of aggregation may persist above the temperature of disappearance of the meniscus and is characterized by a dynamic regional orientation.

Specifically, Mayer and Harrison have predicted the existence of a region above the critical temperature throughout which $\left(\frac{\partial P}{\partial V}\right)_T = 0$. This region has an upper limit at that isothermal for which $\left(\frac{\partial P}{\partial V}\right)_T = 0$ for one point only. The isothermals of Geddes and Maass (4) showed no such region. This can be explained on the assumption that the experimental points of the isobars, from which the isothermals were evaluated, were not taken with sufficiently small temperature increments.

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In the present work, isothermals were determined experimentally at volume intervals as minute as possible, particularly throughout the volume ranges where flat portions of the curves might be expected. Relative pressures are determined to the limit of error that is inherent in the manual thermostatic control of the temperature of the carbon dioxide, that is, 0.01 atm. Within this limit the prediction of Mayer and Harrison has been verified. The data of these and other experiments are given below.

Experimental

The apparatus used in this investigation has been adapted from the original design of Geddes and Maass (4). It consists of two Pyrex glass bombs, supported on brass rods, and connected from the bottoms by a U-tube of heavy walled Pyrex capillary. The apparatus is filled with pure mercury to about the half-way position in each bomb. This mercury acts as a piston in the manipulation of the ethylene, which is confined in the right-hand bomb, and also transmits the pressure generated by the carbon dioxide in the left-hand bomb. The carbon dioxide is added in the proper amount so that a two-phase system will be maintained through the volume and temperature ranges required. In these respects the apparatus of Geddes and Maass has been copied exactly. In the present arrangement, however, the spiral and float have been omitted, and differences in volume are recorded by the position of the mercury level as read upon a cathetometer scale. The internal diameters of the tubes were calibrated by measuring the height of known weights of pure mercury, and were found to be constant within the experimental error of the calibration. The determination of the absolute volume necessitated a geometric estimation of the volume of the draw-off; this was checked by repeating the determination of a point upon the isobars of McIntosh and Maass (5). The agreement was very good.

The absence of the spiral and float permitted the use of much narrower tubing, with consequent decrease in the danger of explosions. The inability with this design, to detect the presence of heterogeneous systems is not a great disadvantage, because the conditions under which these systems exist were well known from previous work, and the pressures of such systems were the point of interest rather than the actual density differences. Moreover, it was now possible to stir the ethylene by means of a magnetic stirring arrangement.

Experimental Results

Five isothermals of the system ethylene were obtained and are represented in Fig. 1 and the values tabulated in Table I. The experimental procedure, the same in all cases, was as follows. The ethylene was compressed to a high density at 8.9° C. by adjustment of the carbon dioxide pressure. The temperature of the ethylene was then raised at constant volume to the temperature of the desired isothermal by balancing the change in pressure by further careful adjustment of the carbon dioxide pressure. After equilibrium had been attained, small decreases in the pressure were made and the equilibrium

TABLE I

Pressure-volume-temperature data

Volume, cc.	Pressure, atm.	Volume, cc.	Pressure, atm.	Volume, cc.	Pressure, atm.
Temperature, 8.92° C.		*Temperature, 9.22° C.*		*Temperature, 9.42° C.*	
2.532	49.93	2.590	50.18	2.710	50.26
2.587	49.73	2.613	50.06	2.735	50.15
2.672	49.54	2.655	49.96	2.838	50.06
2.893	49.45	2.715	49.87	2.950	50.02
3.271	49.45	2.794	49.85	3.176	49.99
3.681	49.46	2.830	49.80	3.300	49.99
4.303	49.38	2.970	49.75	3.550	49.97
4.317	49.34	3.284	49.75	3.723	49.94
		3.666	49.73	3.910	49.90
		3.876	49.72	4.104	49.85
		4.006	49.68		
		4.174	49.65		
Temperature, 9.50° C.		*Temperature, 9.60° C.*		*Temperature, 9.60° C.*	
2.705	50.42	2.695	50.52	4.000	50.10*
2.722	50.32	2.713	50.45	3.958	50.16
2.762	50.22	2.756	50.34	3.903	50.20
2.789	50.19	2.854	50.27	3.782	50.23
2.829	50.17	3.135	50.18	3.586	50.29
2.908	50.12	3.360	50.17	3.148	50.34
2.970	50.10	3.512	50.15	2.858	50.36
3.235	50.08	3.607	50.14	2.753	50.42
3.455	50.07	3.710	50.13		
3.624	50.06	3.859	50.09		
3.857	50.03	4.020	50.05		
4.197	49.90				

* *Increasing pressure, thermal equilibrium only established.*

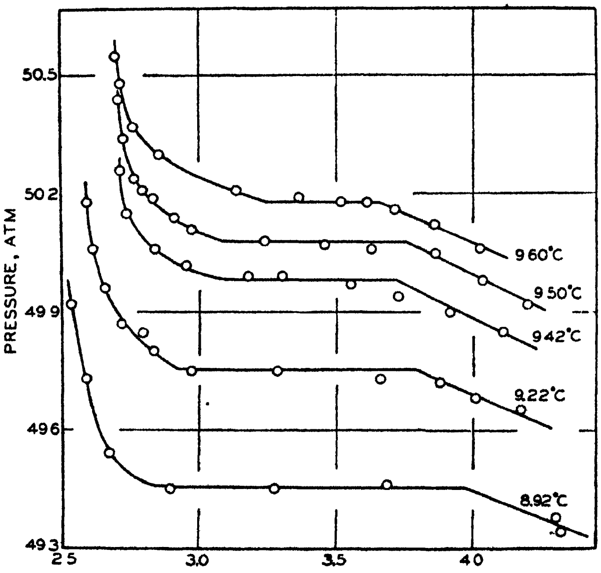

Fig. 1.

volumes determined from the mercury level as read upon the cathetometer scale. In that region where a horizontal part of the curve is shown, the decrease in pressure is exactly compensated for by the change in mercury level.

All isothermals showed a region wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$, although the isothermals at 9.50° C. and 9.60° C. are respectively at and 0.10° higher than the temperature at which the meniscus disappears. The envelope of this region has not yet been completely determined, but insofar as the work has been carried out, the prediction of Mayer and Harrison mentioned above has been verified.

Isothermal at 9.60° C.

Since the deduction of the existence of a two-phase system from the observation of a region wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$ is open to the objection that the behaviour of a one-phase system, if the compressibility is great enough, may simulate that of a two-phase system, and since the compressibility of liquids near the critical point is admittedly enormous, the direction of measurement of the points along the isothermal at 9.60° C. was reversed. That is, when the substance had been expanded to the last point on the isothermal, the pressure was increased. As soon as temperature equilibrium had been established, the pressure was maintained constant for 10 min. By following this procedure, the upper curve of Fig. 2 was obtained. This showed the compressibility of the system to be dependent upon its previous history. That the points of the lower curve are not dependent on the previous condition of the system, provided only that expansion into the true "gaseous" region has not occurred, was shown by repeating, several days later, the determination of a point on the flat portion of the curve. The procedure was as follows. The system was compressed to a high density, the temperature raised as previously described, and the pressure adjusted to the value corresponding to the flat portion of

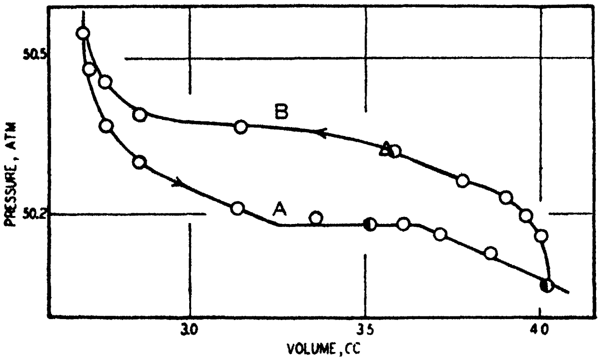

FIG. 2

the curve. Immediate expansion took place, and an equilibrium value was attained at the volume represented by the shaded circle. This point showed no change after more than 15 min. under these conditions. The pressure was then adjusted in order to repeat the last "vapour" point shown upon the diagram. This point (also shaded circle) was exactly repeated, and no tendency to change was exhibited at the end of 15 min.

The question whether the pressure on the higher curve would fall spontaneously to the value on the lower curve was then investigated. After expansion to the "gaseous" region of density the pressure on the system was adjusted to give the triangular point on the upper curve. When this point had been reached, the volume was maintained as constant as possible, and a pressure-time curve obtained. It was found that the pressure fell quite rapidly to the value of the original curve, where it remained constant. The difficulty of keeping the volume constant is very great, as the limit of adjustment of pressure is 0·01 atm , which represents a change of nearly 4 mm. in the height of the mercury. However, the volume can be kept constant enough to show clearly the true trend of the pressure with time The figures are given in Table II.

TABLE II

Volume	Temperature	Pressure	Time
3 59	9 60	50 28	0
3 55	9 60	50 27	7
3 55	9 60	50 24	13
3 55	9 60	50 22	20
3 57	9 60	50 20	26
3 57	9 60	50 18	34
3 57	9 60	50 18	40

NOTE *Zero time was taken at about 12 min after the original pressure adjustment was made*

The information obtained from these experiments indicates the interesting deduction that, as shown by Geddes and Maass, although compression destroys the macroscopic heterogeneity of the system, the two-phase character is re-formed by compression, even at a temperature 0.10° higher than the temperature of disappearance of the meniscus. This leads to the conclusion that over short ranges of temperature above that at which the meniscus becomes invisible, the nature of the system is determined by the density, or the mass-volume ratio Further support of this statement may be derived from the following experiments.

Pressure Measurements of the Heterogeneous and Homogeneous Systems at 9.50° C.

The question of relative stability of the heating and cooling curves of such a typical isochore as appears in Fig. 3, as measured by the pressure of the systems over a range of density from below the critical density to well above it, was determined by the following series of experiments. The volume of the system was fixed by freezing the mercury in the centre U-tube at a value of the average density where a heterogeneous system is known to exist from the previous work of McIntosh and Maass. The temperature of the ethylene was then raised to 9.50° C., the mercury melted, and the pressure of the system corresponding to a point upon the heating curve of the isochore determined.

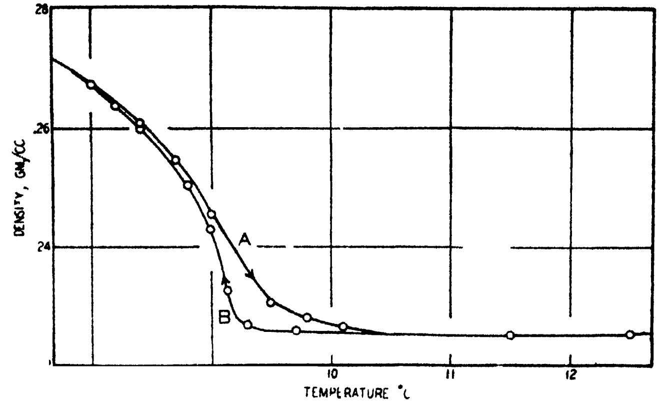

FIG. 3.

The mercury was then frozen, and the temperature raised to 11 5° C., where the density of the system has been shown to be constant. After sufficient time had been allowed for the medium to reach equilibrium, the temperature was again lowered to 9 50° C. and the pressure determined. It was shown that over the range of densities studied, the pressures shown by the upper curve, A, and lower curve, B, are identical, and are the same as the pressure corresponding to the 9 50° C. isothermal of the homogeneous system. The data are given in Table III. The pressures, although recorded to only 0.01 atm., are more nearly equal than 0.01 atm. The reason for this statement is that, although changes in pressure can be determined with any degree of certainty only to that limit, smaller differences in pressure are shown by the change in mercury level on the cathetometer scale. That is, when a pressure measurement had been made during the determination of the heating

TABLE III

Av. Dens.	$Pressure_A$	$Pressure_B$	Temp.
1990	50 08	50 08	9 50
2040	50 08	50 08	9 50
2090	50 08	50 08	9 50
2173	50 08	50 08	9 50
2287	50 08	50 08	9 50

Pressure of flat portion of homogeneous isothermal at 9 50 is 50 07 atm. Range of density of horizontal portion curve, A, the mercury frozen, and the conditions adjusted to give the point upon the cooling curve, B, and the mercury melted, no change in mercury level could be detected by means of the cathetometer.

The agreement between the pressure of the macroscopically heterogeneous system and that corresponding to the horizontal portion of the isothermal of the homogeneous system, together with the further similarity of density range throughout which the heterogeneous system is known to exist on the one hand, and throughout which the pressure of the homogeneous system is known to remain constant on the other hand, indicates that for these temperatures which exhibit horizontal regions on the pressure-volume curves, heterogeneous systems may be obtained, which are apparently stable and will show no tendency to change spontaneously to systems of a homogeneous character.

Further, apparently then, the flat portion of the cooling curve of a typical isochore cannot be regarded as representing a homogeneous gas system with the liquid structure destroyed, for such a gas system would have a pressure independent of the volume over quite appreciable ranges. It is concluded, therefore, that the system, although macroscopically homogeneous, is still a two-phase system, with the effect of the temperature being to disperse, or mix mechanically, the two phases. This opinion is in agreement with the conclusion reached by Naldrett, Mason and Maass from a study of critical opalescence which is to be published shortly. It also explains the observation of McIntosh and Maass (5) that the phase densities of ethylene at the critical temperature are dependent on the mass-volume ratio of the system. From this new point of view, the phase densities will be dependent on the amount of dilution of one phase by the other, which, as the meniscus rises or falls rapidly near the critical temperature, depending upon the value of the average density, will be a function of the mass-volume ratio.

Effect of Mechanical Stirring upon the Pressure of the Heterogeneous System.

In the design of apparatus used in this investigation it was possible to include a magnetic stirring arrangement in the ethylene side of the system. This was done in order to ascertain whether mechanical stirring, which has been emphasized as necessary in criticisms of work done in this laboratory, would affect the phenomena which are observed.

A heterogeneous system was therefore obtained at 9.50° C. and its pressure recorded. This system was then violently stirred by movement of the magnet up and down the length of the tube for a period of 20 sec. Several minutes were allowed to elapse, and the pressure was again recorded. This treatment was repeated four times. No change in pressure could be detected and the mercury level as read upon the cathetometer scale was unchanged. Although no mass movement of material could be detected during the stirring, the stirring was of sufficient violence to cause large visible transfers of liquid short distances into the vapour phase when the temperature was below the critical. This experiment lends strong support to the statement of McIntosh and Maass that "mechanical stirring that does not cause local heating and cooling, or expansion and compression, does not influence the phenomena observed, either in kind or in rate of attainment of equilibrium."

Moreover, the fact that the phenomena reported in this paper, which are similar to those reported in previous publications from this laboratory, was observed in a tube that contained no spiral, completely refutes the argument of Ruedy (4) that the presence of a spiral acts as a deterrent to the proper mixing and diffusing of the system, and is the reason for the anomalous observations that have been made in the critical region.

Apparent Discrepancies between Work of Geddes and Maass and Present Work

A disagreement in the values of the critical pressure of ethylene has been found. Geddes and Maass found that the critical pressure depended upon the mass-volume ratio and reported the two values of 49.98 and 50.01 atm. at the average densities of 0.2056 and 0.2302 gm. per cc. respectively (5). The present work gives a critical pressure of 50.07 atm. over a density range of 0.198 to 0.220 gm. per cc. approximately. No attempt to explain this difference is considered feasible at the present stage of the work.

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SODIUM CHLORIDE SOLUTIONS AS AN ISOPIESTIC STANDARD[1]

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Abstract

A method is described for the accurate determination of the vapour pressure of aqueous solutions of non-volatile salts. Solutions of two salts contained in a large silver dish are rocked in an evacuated desiccator until equilibrium is attained, then the vapour pressure of the one solution is determined from the known vapour pressure of the other. Results on the rate of attainment of equilibrium are given for various types of containers.

Sodium chloride is chosen as the standard. Results are given for the system sodium-chloride–potassium-chloride at 25° C., 30° C., and 35° C. Since there is a disagreement amongst the results for sodium chloride calculated from e.m.f. data and those determined from direct vapour pressure data, an arbitrarily selected vapour pressure curve is adopted. This curve is found to yield the activity coefficients of potassium chloride remarkably well. The method yields results whose accuracy is comparable with that of the best e.m.f. measurements.

Introduction

The thermodynamic properties of a solution of an electrolyte may be obtained from various equilibrium measurements and conveniently expressed in terms of the Lewis and Randall (11) activity coefficient.

The measurements capable of the greatest accuracy have been the lowering of the freezing point, raising of the boiling point, osmotic pressure, solubility, electromotive force, and vapour pressure. Each of these methods possesses particular advantages under certain conditions. The study of the vapour pressure of aqueous solutions of electrolytes and non-electrolytes is probably the most direct laboratory procedure, for, in this method, unlike that of the freezing point depression and boiling point elevation, the temperature may be varied as desired, and thus the use of thermal data eliminated to some extent. Moreover, it possesses the advantage over the method of e.m.f. measurements in that there is no necessity of finding suitable reversible electrodes. The results of these various methods show conclusively that no equilibrium measurement can be carried out in concentrated solutions with the accuracy obtainable in a vapour pressure determination.

An historical review of the various methods devised up to 1928 has been given by Pearce and Snow (15). Since that time Hill (7) has described a method depending on the principle of the wet and dry bulb thermometer which has been applied to biological work. Lannung (10) has described a

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Contribution from the Department of Chemistry, University of Toronto, Toronto, Canada.
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method whereby the vapour pressures of aqueous solutions were measured by the change in resistance of a hot wire. The accuracy of these two methods however is not comparable to the precise work of Lovelace, Frazer, and Sease (12) and their students who used a static method.

The apparatus and technique of the classical static and dynamic methods are cumbersome and laborious as compared to the isopiestic method first utilized by Bousfield (2). However, from the nature of Bousfield's procedure it was impossible that thermal and pressure equilibria could exist simultaneously between the liquids, although it was not impossible that the composition of the solutions might in time become approximately isopiestic. Sinclair (25) has to a great extent eliminated the difficulties encountered by Bousfield (2), so that the method may yield, within a reasonable time, results of the highest accuracy.

Theoretical Considerations

Bousfield (2) first pointed out that the rate of attainment of pressure equilibrium in his apparatus depended on the rate of attainment of temperature equilibrium. I C.T. (9) give 1 4 mm. per degree as the value of dp/dt for water at 25° C. Since the value of dp/dt for dilute aqueous solutions is approximately the same, two solutions whose vapour pressures differ by 0 001 mm. when they are at the same temperature owing to a difference in concentration would have the same vapour pressure if the temperature of the stronger solutions was only 0 0007° C. higher than that of the weaker. At 25° C. the latent heat of vaporization of water is 2436 Joules per gm ; consequently the time for 1 gm. to distil, or for 2436 Joules to flow from one solution to another separated by a medium of thermal conductance equivalent to a centimetre cube of copper, and under a thermal head of 0 0007° C., was calculated by Sinclair (25) to be 10 days. Similarly, he calculated that for glass the time necessary was 10 years. For silver, the time would be only nine days. It would be necessary, therefore, for the method to be practical, to have very good thermal conduction and small quantities of water distilling. Bousfield (2) obtained very good results with glass vessels. This may be explained by the fact that he actually allowed the solutions to approach equilibrium over a period of months, although he stated that a few days would be sufficient. His method was too slow for use when very accurate results were desired.

Sinclair (25) incorporated the following principle:—

Good metallic conduction between the two solutions to reduce thermal resistance. This included:—

(a) Material and type of block,

(b) Nature of contact between the block and the dishes containing the solution.

The factors left were:—

(1) Diffusion of solute,

(2) Conduction of heat through the solution,

(3) The amount of heat to be transferred.

This principle of good conduction cannot be overemphasized, because this is the condition that must be fulfilled in any comparative vapour pressure measurement. For example, if the activity coefficient of potassium chloride is to be determined with the same precision as is possible in an e.m.f. measurement, it is essential that the solutions must not differ in temperature, when equilibrium is attained, by more than 0.00007° C. This corresponds to a difference in pressure of 0.0001 mm. However, the closeness of this approach to a temperature equilibrium does not imply that the temperature of the system as a whole must be held within these limits. In Sinclair's work (and in the writers') the bath temperature was held to only 1/100th of a degree, but a thick glass desiccator tended to "damp out" the bath fluctuations, in so far as they would affect the metal block which was the chief conducting medium between the solutions. To insure a uniform temperature throughout this block, a metal of high thermal conductivity was chosen. Sinclair (25) used copper and also small quantities of shallow solutions to eliminate the remaining factors.

Experimental and Results

Types of Containers

Sinclair (25) used four silver-plated copper dishes, $1\frac{1}{2}$ in. square and $\frac{3}{4}$ in. deep, placed in four holes in a heavy, silver-plated copper block, which in turn was placed in a glass desiccator. The crevice between a dish and the block was filled with sodium hydroxide solution of approximately the same concentration as the solution in the dishes. At the conclusion of an experiment the sodium hydroxide was washed off with a stream of cold water. Sinclair's use of sodium hydroxide introduced a possible source of error, and to overcome this, in most of the writers' experiments, the block itself was made the dish, the holes containing the solutions. In the preliminary experiments a copper dish was used which was internally silver-plated to eliminate the corrosive action of the chloride solutions. This dish had a base of electrolytic copper $\frac{1}{16}$ in. thick and 7 in. in diameter, to which was brazed a vertical collar $\frac{1}{16}$ in. thick and $1\frac{1}{2}$ in. high, also of electrolytic copper. The inside was divided into four compartments by means of two strips of copper brazed into place, and the whole dish was then silver-plated. It was found to weigh about 1200 gm. Ten cubic centimetres of solution was used in each compartment. Since the main difficulty proved to be chemical action at the cracks, the collar and base were spun out of one piece of electrolytic copper. But even this showed signs of chemical action in the presence of chloride solutions The actual corrosion was slight and confined to pin holes chiefly at the compartment joints, but nevertheless it could not be overlooked in precise work.

A solid silver dish was made from a block of silver (99.97% pure) $7\frac{1}{4}$ in. in diameter and $1\frac{1}{2}$ in. high, in which four holes were machined. Each hole was $2\frac{13}{16}$ in. in diameter and $1\frac{5}{16}$ in. deep and separated from the others at the nearest point by $\frac{1}{8}$ in. of silver. The dish was internally gilded and weighed 5255 gm. This dish was found to be entirely satisfactory and it was used for the system sodium-chloride–potassium-chloride.

Small silver dishes were used with a procedure similar to that of Robinson and Sinclair (21). These spun dishes were solid silver (99.97% pure) and gold-plated inside and out. The tapers of the dishes fitted into holes in a solid block of silver-plated electrolytic copper which was 7¾ in. in diameter and 1 in. thick. The dishes were fitted with removable lids which were made to fit quite snugly to eliminate evaporation. The lids also had lugs for handling. Four dishes were used. Each dish and lid weighed 58 gm. Fig. 1 shows the dimensions and shape of a small silver dish.

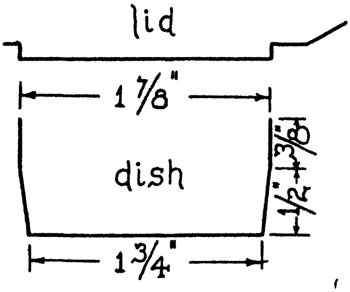

FIG. 1. *A small silver dish.*

The copper and silver blocks were placed in heavy-walled, glass vacuum desiccators, which in turn were placed in water baths.

Materials and Method of Analysis

Conductivity water was used; 20 cc. left a residue of less than one-tenth of a milligram.

The sodium and potassium chlorides were Kahlbaum's "zur analyse mit garantieschein". Isopiestic experiments showed that recrystallization of these salts did not affect the results.

PROCEDURE WITH THE LARGE SOLID SILVER DISH

Ten cubic centimetre portions of the solution were pipetted into each compartment of the dish after it was placed in the desiccator. Duplicates of each solution were placed in diagonally opposite compartments. The desiccator was immersed in the bath and then evacuated by means of a Hyvac pump for exactly eight minutes. This was found by a preliminary experiment to be the time necessary to evacuate the empty desiccator to a pressure of about 2 mm. of mercury. The solutions were then rocked for a definite length of time, which was generally between one and two days when the solutions were 1 *m* or stronger, between two and three days for solutions of concentrations between 0 5 and 1 *m*, and three days or more, when the concentration was less than 0.5 *m*.

At the end of an experiment, the pressure in the desiccator was again determined in order to detect any leakage that might greatly retard the rate, and then the desiccator was removed from the bath. Air was admitted through a U-tube containing cotton wool and calcium chloride to eliminate dust and grease and prevent condensation. The desiccator lid was then removed and the solution in each compartment transferred, by means of clean dry pipettes, to weighing bottles. The solutions were weighed and the salt content was determined by heating to constant weight at 150° to 160° C. after evaporating to dryness in an electric oven at 95° C. The solution losses due to evaporation prior to weighing were negligible as the solutions were exposed to the air for only about one minute. The final weights were reduced to *in vacuo* and corrected for the residual moisture in the salt.

THE CORRECTION FOR THE RESIDUAL MOISTURE IN THE SODIUM AND POTASSIUM CHLORIDES

In order to obtain this correction it was necessary to determine the temperatures at which the last traces of moisture were removed. Since the glass weighing bottles could not be used above 300° C., the residual salt which was first heated to an approximate constant weight at 150° C. in a gas oven, was then transferred in part to a platinum crucible, and reheated to constant weight in a high temperature electric oven. The platinum crucibles were used with loose fitting lids and were placed inside a beaker, having no spout, which was covered with a watch glass. The former eliminated spurting of the salt and the latter promoted ease of handling. The temperature of the oven was measured with a chromel-alumel thermocouple. Samples of the actual residual salt from various isopiestic experiments were heated to different temperatures. Table I represents the results of a typical experiment with sodium chloride. A series of experiments was conducted; Table II shows the final percentage loss in weight of the sodium chloride on being so heated.

TABLE I

WATER CONTENT OF THE SODIUM CHLORIDE AT VARIOUS TEMPERATURES

Weight of sodium chloride taken = 1 6772 gm.

Temp., °C.	Total time of heating, hr.	Weight of crucible and salt	Loss in weight of salt, %
	0	40 8182	
215	4	40 8180	
215	21	40.8177	0.03
600	26	40 8154	0.17
600	42	40 8152	0 18
600	59	40 8154	0.17

TABLE II

WATER CONTENT OF SODIUM CHLORIDE

Temp., °C.	Total time of heating, hr.	Weight of sodium chloride taken, gm.	Loss in weight of of salt, %
600	8	0.5424	0.17
600	11	1 7687	0.21
600	21	2.1590	0.19
700	10	0 9718	0.22

Average percentage loss, 0.19%.

Thus in the case of the sodium chloride, since the moisture correction was found to be constant on heating to 600° C. it appeared justifiable to heat the salt to constant weight at 150° C. and then apply a constant correction to this weight for the residual moisture.

In the case of the potassium chloride it was found impossible to obtain an absolutely constant weight at 150° C.; consequently, the salt was heated for 24 hr. at 150° C. and then used in the experiments the results of which are given in Tables III and IV, which are analogous to Tables I and II.

TABLE III

WATER CONTENT OF THE POTASSIUM CHLORIDE AT VARIOUS TEMPERATURES

Weight of potassium chloride, 1 3648 gm.

Temp., °C.	Total time of heating, hr.	Weight of crucible and salt, gm.	Loss in weight of salt, %
	0	44 2346	
215	4	44 2331	0 11
215	21	44 2314	0 23
600	26	44 2309	0 27
600	42	44 2305	0 30
600	59	44 2300	0 34

TABLE IV

WATER CONTENT OF THE POTASSIUM CHLORIDE

Temp., °C.	Total time of heating, hr.	Weight of potassium chloride taken, gm.	Loss in weight of salt, %
600	10	1 2152	0 25
600	11	1 4498	0 25
650	21	1 4450	0 26

Average percentage loss, 0 26%.

Since the moisture correction for potassium chloride that had been heated for 24 hr. at 150° C. was decreased by a constant amount when the salt was given an additional heat treatment at 600° C., it appeared justifiable to heat the potassium chloride for 24 hr. at 150° C. and then apply a constant correction to this weight for the residual moisture.

From Table III above, it would appear possible to dry potassium chloride at a temperature not greatly in excess of 215° C. for a period of one day or more. Other experiments showed that the same purpose was accomplished at 650° C. in two or three hours, but at 650° C. prolonged heating causes a slight but continuous loss of the potassium chloride. This is probably due to the evaporation of the salt. From the data in I. C. T. (9) an estimation of the vapour pressure of the liquid phase shows that the vapour pressure of potassium chloride is roughly three times as great as that of sodium chloride at 1000° C. Recently Mayer and Wintner (13) measured the actual vapour pressures of solid sodium and potassium chlorides, and found the vapour pressure of potassium chloride to be roughly three times that of sodium chloride at about 650° C. Since the rate of evaporation is proportional to the pressure, the potassium chloride would evaporate about three times as fast as the sodium chloride; this is in qualitative agreement with the writers' results.

The method of analysis developed for the sodium and potassium chlorides yielded concordant results, but does not of itself ensure that all the water had been eliminated from the salt. Richards and Hall (18) prepared anhydrous sodium chloride by fusing the salt in a closed platinum crucible, and then evaporated to dryness known weights of this anhydrous salt which had been dissolved in water. They found that this gave an apparently constant weight after a few hours of heating at 150° C., but this residue was found to weigh on an average 0 73% more than the fused salt. They also found that if the solution was evaporated at 150° to 160° C., precautions being taken to prevent spattering, and then thoroughly dried at 300 to 310° C., the weight of salt so found agreed to within 0 05% of the original weight. They do not recommend this method for analyses. The method apparently depends on the size of the crystal formed, the smaller the crystal size the less rigidly the water is held. The writers believe, however, that all the bound water in their sodium chloride was released by heating to 600° C., because experiments conducted by Allgood (1), on the determination of the concentration of a silver nitrate solution by means of a differential potentiometric titration, known weights of sodium and of potassium chlorides previously heated to 650° C. being used, yielded, to within 0.05%, the same concentration for the silver nitrate In one case the potassium chloride was even fused, whereas the sodium chloride was granular, and the results still checked.

PROCEDURE WITH THE SMALL SILVER DISHES

In the case of the small silver dishes the concentration was obtained from the known weight of salt originally put in the dish and the final weight of the solution. The agreement of the duplicates was an indication of the attainment of equilibrium since they were each originally of different concentrations.

RATE OF ATTAINMENT OF EQUILIBRIUM WITH VARIOUS TYPES OF CONTAINERS

A comparison was made of the rate of attainment of equilibrium in the various dishes. For this purpose 1.48 *m* and 2.00 *m* sodium chloride solutions were used in the silver-plated copper dish and in the silver dish. There was weighed into the small silver dishes an amount of salt which yielded solutions of concentrations approximately equivalent to those above when 4 cc. of conductivity water was added. In Series *A* and *B* (see Table V) the small silver dishes were used, Dishes (1) and (3) contained the stronger solution and Dishes (2) and (4) the weaker. In each case the total volume of the solution per dish was 4 cc. In *A* there was no liquid between the dishes and the block, while in *B* there was about 2 cc. of approximately 1.75 *m* sodium chloride solutions. Series *C* and *D* were carried out in the silver-plated copper dish and the silver dish respectively, with 10 cc. of solution per compartment. Here again the stronger solutions were in compartments (1) and (3) and the weaker solutions in (2) and (4). The results of the analyses of the solutions after shaking for 24 hr. in the thermostat are summarized in Table V, which is self-explanatory.

TABLE V

RESULTS WITH VARIOUS CONTAINERS AFTER 24 HR. AT 30° C.

No.	Weight of salt per gram of solution				Average of		Diff. of (a) and (b), %
					(a)	(b)	
	(1)	(2)	(3)	(4)	(1) and (3)	(2) and (4)	
A	0.08349	0.08166	0.08375	0.08160	0.08362	0.08163	2.5
B	0.09419	0.09417	0.09439	0.09426	0.09429	0.09422	0.07
C	0.09324	0.09334	0.09334	0.09368	0.09329	0.09351	0.2
D	0.09137	0.09120	0.09146	0.09124	0.09142	0.09122	0.2

From *A* and *B* it can be seen that the presence of the solution between the dish and the block greatly hastened the rate. However, in *A*, the dishes were again placed in the desiccator, the latter evacuated, and the dishes were rocked for an additional 24 hr., and at the end of this second period the percentage difference between the average of (1) and (3) and the average of (2) and (4) had fallen to 0.02%; consequently, no liquid was used between the dish and the block in the later experiments. In the experiments listed in Table V the final concentration was about 1.75 *m*; therefore a final concentration difference of 2% corresponded to a vapour pressure difference of 0.02 mm. and similarly a final concentration difference of 0.1% corresponded to a vapour pressure difference of 0.001 mm. Thus the method was capable of yielding vapour pressures to a greater accuracy than that obtained in any absolute measurement. The initial concentrations here differed by 25%, but if the original solutions had differed only by 1 or 2% from isopiestic concentration, equilibrium would have been attained with the silver dish within the same time as that used for the small silver dishes, and since 10 cc. of solution was used the analysis was capable of greater accuracy.

With the silver-plated copper dish the solutions in all the compartments except the second were turbid, showing the presence of a precipitate, probably silver chloride. This would explain the fact that the solutions which were originally the stronger were now the weaker. The two duplicates for the silver-plated copper dish agreed to within 0.2% and, therefore, the rate was as fast as that for the silver dish which weighed five times as much as the silver-plated copper dish. This would lead one to believe that a very massive copper or silver block was not necessary to obtain concordant results at these concentrations.

CONCENTRATION OF ISOPIESTIC SOLUTIONS OF POTASSIUM AND SODIUM CHLORIDES

Table VI summarizes the results obtained at 25°, 30°, and 35° C. respectively. Here m_1 and m_2 are the molalities of isopiestic solutions of potassium and sodium chlorides respectively. Each of the concentrations given is the mean of two duplicates agreeing in general to within 0.1% of each other.

TABLE VI

ISOPIESTIC CONCENTRATION OF POTASSIUM CHLORIDE SOLUTIONS

KCl m_1	NaCl m_2	m_2/m_1	KCl m_1	NaCl m_2	m_2/m_1
Temperature, 25° C.					
4.756	4.167	0.8761	0.6101	0.5941	0.9738
4.218	3.741	0.8869	0.6063	0.5901	0.9733
3.812	3.410	0.8945	0.5166	0.5047	0.9770
3.005	2.737	0.9108	0.4235	0.4147	0.9792
2.687	2.469	0.9188	0.3050	0.2997	0.9826
2.193	2.042	0.9309	0.3195	0.3148	0.9853
1.475	1.399	0.9486	0.2125	0.2103	0.9897
1.0390	0.9962	0.9588	0.1990	0.1976	0.9930
0.8865	0.8553	0.9648	0.1087	0.1088	1.0009
Temperature, 30° C.					
4.479	3.948	0.8815	0.8363	0.8086	0.9669
4.057	3.611	0.8900	0.7651	0.7432	0.9714
3.717	3.337	0.8977	0.6255	0.6095	0.9744
3.375	3.052	0.9043	0.4878	0.4767	0.9772
2.835	2.596	0.9159	0.4468	0.4388	0.9821
2.334	2.167	0.9283	0.3102	0.3050	0.9832
1.578	1.493	0.9461	0.1975	0.1961	0.9929
1.073	1.030	0.9599	0.1033	0.1031	0.9981
Temperature, 35° C.					
4.773	4.201	0.8801	0.8789	0.8483	0.9651
4.243	3.765	0.8874	0.7743	0.7493	0.9677
3.796	3.404	0.8967	0.6157	0.6004	0.9751
3.161	2.874	0.9092	0.5122	0.5020	0.9801
2.685	2.471	0.9204	0.4099	0.4024	0.9818
2.173	2.025	0.9318	0.3064	0.3022	0.9863
1.493	1.420	0.9512	0.2068	0.2053	0.9927
1.059	1.017	0.9597	0.1047	0.1045	0.9981

From the graph in Fig. 2 values of m_2/m_1 were obtained for round values of m_1. Since there is very little change in the results at the various temperatures, the ordinate scale in Fig. 2 is lowered one square for each succeeding curve.

Discussion

The Selection of the Vapour Pressure Curve for Aqueous Sodium Chloride Solutions

In the isopiestic method the vapour pressure of one solution must be accurately known in order to determine the vapour pressure of any other solution. The method, therefore, depends on knowing the vapour pressure lowering of any one salt used as a standard. One must arbitrarily choose a suitable standard, and the authors propose sodium chloride for this purpose, because very accurate measurements on colligative properties have been done on only a few substances, and sodium chloride has been subjected to almost all these measurements. Robinson and Sinclair (21) chose potassium chloride as the standard, but sodium chloride is more soluble and therefore gives a greater range of concentration. Moreover Rossini (22) has stated that the calorimetric data on sodium chloride are more reliable and comprehensive than those for any other salt. It also has been found possible to heat sodium chloride to constant weight at 150° C. and then apply a correction for the remaining water.

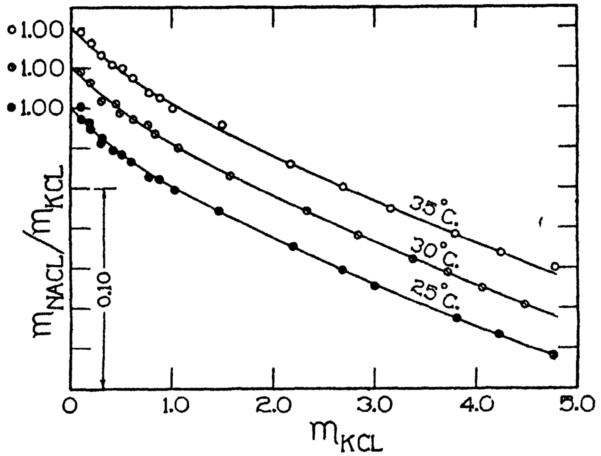

FIG. 2. *The ratio of the molality of the sodium chloride to the isopiestic molality of the potassium chloride.*

In the tabulation of vapour pressure data the most convenient quantity is R which is closely related to the activity coefficient. If μ_1 be the chemical potential of the solvent then

$$\mu_1 - \mu_1^0 = R_1 T \ln a_1 = R_1 T \ln (1 - Rm) \tag{1}$$

where μ_1^0 stands for the chemical potential in its standard state, a_1 the activity of the solvent, R_1 the gas constant, T the absolute temperature, and m the molality, i.e., the concentration expressed as moles of solute per 1000 gm. of solvent.

If the vapour of the solvent acts as a perfect gas, then

$$a_1 = P/P_0 \tag{2}$$

where P_0 is the vapour pressure of the solvent in the standard state (in the writers' case, pure water), and P is the vapour pressure of the solution.

Thus from Equations (1) and (2)

$$R = \frac{1 - a}{m} = \frac{P_0 - P}{mP_0} \tag{3}$$

Robinson and Sinclair (21) have pointed out the discrepancies that exist amongst the values of R for potassium chloride calculated from e.m.f. measurements, boiling points, freezing points, and those obtained directly from vapour pressure measurements. They, accordingly, made an arbitrary choice for the osmotic coefficient curve of potassium chloride, being guided mainly by the e.m.f. data for solutions of concentration less than 1 *m* and the vapour pressure data for the higher concentrations.

The writers have omitted the boiling point and freezing point data and have chosen R for sodium chloride from the remaining two sources. Our reason for so doing is that in spite of the accuracy of the freezing point and boiling point data as such, errors in R can be introduced by the temperature correction over such a range. Since the correction is larger for the more concentrated solutions, such values of R for 1 *m* and stronger solutions cannot be very reliable. Thus, the writers' values of R for sodium chloride are chosen from:

(a) The e.m.f. measurements of Harned and Nims (6) at 25° C. which are converted into values of R by means of the relation

$$-\ ln(1 - Rm) = \frac{2}{55.51}\int_0^m md\ ln\gamma\ m = \frac{2m}{55.51} + \frac{2}{55.51}\int_0^m md\,ln\ \gamma, \quad (4)$$

where γ is the activity coefficient of sodium chloride in aqueous solutions.

(b) The direct vapour pressure measurements of Negus (14) and of Gibson and Adams (4), both at 25° C., which yield R directly.

The second column of Table VII gives the values of R computed from the e.m.f. data of Harned and Nims (6) by means of Equation (4). The third and fourth columns give the values of R from the vapour pressure data of Negus (14) and of Gibson and Adams (4), respectively.

It will be observed that for 1.5 *m* the values of R from the e.m.f. and vapour pressure data are in agreement. Since direct vapour pressure measure-

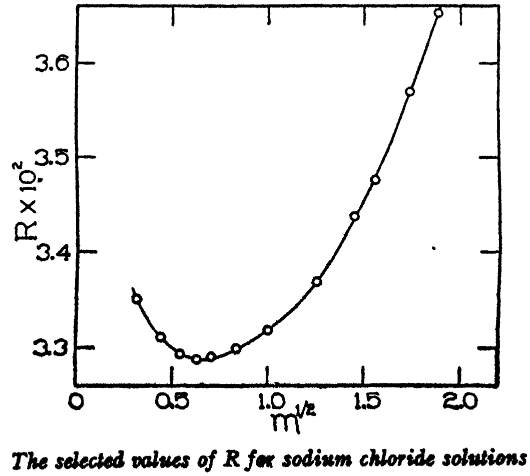

FIG. 3. *The selected values of R for sodium chloride solutions at 25° C.*

ments on dilute solutions are extraordinarily difficult, and, since e.m.f. measurements on concentrated solutions are sometimes unreliable, owing to the solubility effect at the electrodes, the selected values of *R* given in the fifth column are those from e.m.f. measurements taken at concentrations up to 1.5 *m* and from vapour pressure measurements at higher concentrations. Fig. 3 shows the final form of the selected *R* curve, where the abscissa is the square root of the molality.

TABLE VII

THE SELECTED VALUES OF *R* AT 25° C. AND THE CORRESPONDING VALUES OF THE ACTIVITY COEFFICIENT FOR SODIUM CHLORIDE

m	e.m.f. $R \times 10^5$	Negus $R \times 10^5$	Gibson and Adams $R \times 10^5$	Selected $R \times 10^5$	25° C. $-\log \gamma$	30° C. $-\log \gamma$	35° C. $-\log \gamma$
0.1	3351	3294		3351	0.1089	0.1096	0.1105
0.2	3311	3280		3311	0.1355	0.1362	0.1371
0.3	3293	3271		3293	0.1509	0.1514	0.1524
0.4	3288	3265		3288	0.1611	0.1614	0.1622
0.5	3290	3264		3290	0.1680	0.1681	0.1688
0.7	3299	3274		3299	0.1765	0.1762	0.1765
1.0	3318	3305		3318	0.1829	0.1821	0.1819
1.5	3361	3358		3361	0.1835	0.1818	0.1809
2.0	3432	3420		3420	0.1761	0.1737	0.1723
2.5	3503	3489		3489	0.1634	0.1605	0.1588
3.0	—	3566		3566	0.1465	0.1433	0.1412
4.0	—	3724		3724	0.1051	0.1016	0.0994
5.0	—	3879	3895	3895	0.0536	0.0504	0.0486
6.0	—	3990	4005	4005	0.0050	0.0022	0.0012

Table VII also gives the corresponding values of the common logarithm of the activity coefficient ($-\log \gamma$). Up to concentrations of 1.5 *m* at 25° C. they are simply Harned and Nims' (6) observed activity coefficients adjusted to the value of Brown and MacInnes (3) at $m = 0.1$. The latter state that if this is done the two sets of data coincide up to $m = 0.5$.

Harned and Nims (6) represented their activity coefficients by the conventional extended Debye-Hückel relation

$$-\log \gamma = \frac{\mu\sqrt{c}}{1 + A\sqrt{2c}} - B \,.\, 2c + \log\,(1 + 0.036m) \qquad (5)$$

where $\mu = 0.5067, A = 0.837$ and $B = 0.0316$.

This equation however does not represent their results within their apparent limit of error for concentrations above 1 *m*. Consequently the values of $\log \gamma$ at 25° C. in Table VII and those used in effecting the tabular integration in Equation (4) are their experimental ones and not those given by Equation (5). For concentrations greater than 1.5 *m* the activity coefficient of the sodium chloride was obtained from the relation (17)—

$$\log \gamma \Big|_{m} - \log \gamma \Big|_{m=1\cdot 5} = -\frac{h}{2.303}\Big|_{m=1\cdot 5}^{m} - \frac{2}{2.303}\int_{\sqrt{m}=\sqrt{1\cdot 5}}^{\sqrt{m}} \frac{h}{\sqrt{m}}\, d\sqrt{m} \tag{6}$$

where $h = \dfrac{55.51}{2m}\, ln\, a_1 + 1.$

These tabulated values of γ for sodium chloride are in substantial agreement with those that were recently obtained by Robinson (20) from his revised curve of γ for potassium chloride.*

The values of log γ at 30° C. were obtained from the values at 25° C. by the familiar relation

$$\frac{\partial\, ln\, \gamma}{\partial T} = \frac{-\overline{L}_2}{2R_1T^2} \tag{7}$$

where $\overline{L}_2$ is the partial relative molal heat content of the sodium chloride, a quantity that is known to a high degree of accuracy from the work of Robinson (19) and Young and Vogel (26). Integration of Equation (7) gives

$$\log \gamma|_{T''} - \log \gamma|_{T'} = \tfrac{1}{2}\,[-\,\overline{L}_2|_{T''}\ (y) + \overline{C}_{p_2} - \overline{C}^{\circ}_{p_2}(z)] \tag{8}$$

$$\text{where } \frac{T'' - T'}{2.303R_1T''T'} = y \text{ and } T''(y) - \frac{1}{R_1}\log\frac{T''}{T'} = z \tag{9}$$

The values of y and z were taken from the tables of Lewis and Randall (11), and $\overline{C}_{p_2} - \overline{C}^{\circ}_{p_2}$ are the partial molal heat capacities of sodium chloride in aqueous solutions at the concentrations m and infinite dilution respectively. Values of $\overline{C}_{p_2} - \overline{C}^{\circ}_{p_2}$ were obtained from the data of Randall and Rossini (16).

The writers realize that these values of log γ are arbitrarily selected but it is believed that they are the most reasonable choice that can be made at the present time.

Calculation of the Activity Coefficient of Potassium Chloride

Robinson and Sinclair (21) first showed that since the activity of the water is the same in isopiestic solutions, then

$$\partial\, ln\, \gamma_1\, m_1 = \frac{m_2}{m_1}\, \partial\, ln\, \gamma_2\, m_2 \tag{10}$$

where m_1 = the molality of the potassium chloride solution
m_2 = the molality of the sodium chloride solution
γ_1 = the activity coefficient of the potassium chloride
γ_2 = the activity coefficient of the sodium chloride.

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* *Following his visit to the writers' laboratory, Dr. R. A. Robinson of Auckland, New Zealand, undertook to repeat the earlier work done in his laboratory on the system potassium-chloride–sodium-chloride while the writers continued the present investigation. It was hoped that thus it might be possible to eliminate certain minor discrepancies that existed between the various sets of results and to place the question of suitable standards on a firmer basis. The writers wish to thank Dr. Robinson for his active co-operation and for access to his unpublished results.*

This may be written after integrating as

$$\ln \gamma_1 = \ln \frac{m_2}{m_1} + \ln \gamma_2 + 2 \int_0^{\sqrt{\gamma_2 m_2}} \frac{\left(\frac{m_2}{m_1} - 1\right)}{\sqrt{\gamma_2 m_2}} \, d\sqrt{\gamma_2 m_2} \qquad (11)$$

The values of m_2/m_1 were read from Fig. 2 at round concentration of m_1. The

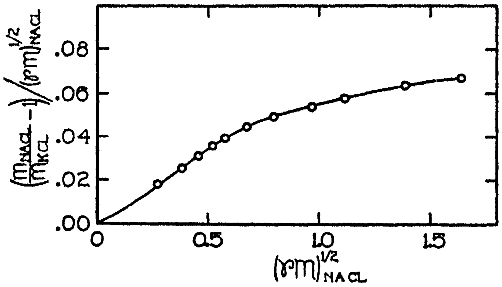

FIG. 4. *The evaluation of the integral* $\int \frac{\frac{m_2}{m_1} - 1}{\sqrt{\gamma_2 m_2}} \, d\sqrt{\gamma_2 m_2}$.

corresponding values of γ_2 at these temperatures were obtained from a large scale plot of γ_2 against m_2. The integral, which is the area under the curve when $\frac{m_2/m_1 - 1}{\sqrt{\gamma_2 m_2}}$ is plotted against $\sqrt{\gamma_2 m_2}$, was evaluated by a graphical integration method (counting squares). Table VIII gives values of log γ_1 computed by means of Equation (11), and, for comparison, the results of other workers.

TABLE VIII

ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE AT 25° C.

KCl m_1	NaCl/KCl m_2/m_1	*a* γ	*b* γ	*c* γ	*d* γ
0.1	0.9950	0.771	0.769	0.770	0.770
0.2	0.9903	0.719	0.719	0.719	0.719
0.3	0.9859	0.688	0.688		0.688
0.4	0.9813	0.667			
0.5	0.9775	0.651	0.651	0.652	0.652
0.7	0.9701	0.628	0.628		0.627
1.0	0.9609	0.606	0.606	0.607	0.605
1.5	0.9481	0.586	0.585		0.584
2.0	0.9354	0.576	0.576	0.578	0.575
3.0	0.9120	0.573	0.571	0.574	0.573
4.0	0.8908	0.582	0.579	0.581	0.581

a *Values obtained in the present investigation.*
b *Values obtained by Harned and Cook (5).*
c *Values obtained by Shedlovsky and MacInnes (24).*
d *Values obtained by Robinson and Sinclair (21) from their arbitrary vapour pressure curve with the value of* γ *at* $m = 0.1$ *adjusted by the writers to coincide with that of Shedlovsky and MacInnes.*

In Table IX the results are given for the activity coefficient of potassium chloride at 25°, 30°, and 35° C. and compared with those of Harned and Cook (5).

TABLE IX

VALUES OF γ FOR POTASSIUM CHLORIDE AT VARIOUS TEMPERATURES

m	25° C.		30° C.		35° C.	
	γ^a	γ^b	γ^a	γ^b	γ^a	γ^b
0.1	0.771	0.769	0.770	0.768	0.768	0.767
0.2	0.719	0.719	0.718	0.718	0.717	0.717
0.3	0.688	0.688	0.689	0.687	0.686	0.685
0.4	0.667	—	0.667	—	0.667	—
0.5	0.651	0.651	0.652	0.651	0.652	0.648
0.7	0.628	0.628	0.631	0.629	0.630	0.626
1.0	0.606	0.606	0.608	0.604	0.610	0.604
1.5	0.586	0.585	0.588	0.585	0.590	0.585
2.0	0.576	0.576	0.580	0.578	0.581	0.579
3.0	0.573	0.571	0.578	0.573	0.580	0.574
4.0	0.582	0.579	0.588	0.582	0.592	0.584

[a] *Present investigation.*

[b] *Harned and Cook (5).*

From Table VIII it can be seen that the values of γ obtained for potassium chloride at 25° C. are in remarkable agreement with the results of Harned and Cook (5) and Shedlovsky and MacInnes (24). The greatest difference corresponds to 0.06 millivolt on the e.m.f. measurements except for 4.0 m, where the difference is 0.13 millivolt. Since for concentrations greater than 1.5 m the γ's chosen for the sodium chloride are obtained from vapour pressure data, the agreement here is an indication of the agreement between vapour pressure data and the results from e.m.f. work. It also shows that the error due to the solubility of silver chloride is negligible in the case of potassium chloride at 25° C.

From Table IX it can be seen that as the temperature increases the two sets of data diverge. The divergence is appreciable for concentrations greater than 1.5 m at 30° C. and greater than 0.5 m at 35° C. The maximum difference corresponds to 0.6 millivolt. This may be due in part to the method of smoothing their data that Harned and Cook (5) employed and in part to the thermal data used in computing the values of the activity coefficient at the higher temperatures. This point can be easily settled when the e.m.f. measurements for sodium chloride at 30° C. and 35° C. are made, by means of cells with transference below 0.1 m.

Since this paper was prepared for publication, the isotonic results of Scatchard, Hamer, and Wood (23) have been published. Their ratios of m_{KCl}/m_{NaCl} *at 25° agree with the writers' ratios to within 0.05% in the range 1.5 to 4* m_{NaCl} *and to within 0.1 to 0.2% from 0.4 – 1.5* m_{NaCl} *which indicates the potentialities of the experimental methods. The reference curves chosen for sodium chloride at 25° agree to within 0.002 in* γ *for concentrations of 1* m *and 5* m *when the values of gamma are adjusted to coincide at 0.1* m*. The gamma curves for potassium chloride at 25° agree to 0.001 for concentrations from 0.1 to 1* m*, and their values for 2, 3, and 4* m*, which are respectively, 0.571, 0.566, and 0.575, may be compared with the values given in Table VIII.*

Acknowledgement

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THE EFFECT OF COMPRESSION ON THE HOMOGENEOUS SYSTEMS ETHYLENE AND AIR-ETHYLENE IN THE CRITICAL REGION[1]

By R. L. McIntosh[2], J. R. Dacey[3], and O. Maass[4]

Abstract

The effect of compression, due to the thermal expansion, on the density of the systems ethylene and air-ethylene in the critical region has been studied. Apparently stable heterogeneous systems, as detected by density measurements, are re-formed by this treatment. The significance of these experiments in relation to critical phenomena is discussed, and an explanation based on a concept of the mutual dispersion of the two phases is suggested.

Introduction

In a recent note (1) from these laboratories, it was pointed out that a means of re-establishing a heterogeneous system from a homogeneous one above the classical critical temperature had been obtained for the first time. Previous to this discovery it had been established that a heterogeneity can persist above the critical temperature, and that this heterogeneity may be destroyed by raising the temperature of the system above the critical temperature and then reproducing the original temperature, or by isothermal expansion or compression to "vapour" or "liquid" densities respectively, or by violent stirring by means of temperature gradients, which has been designated for convenience as "molecular stirring". The present paper deals with the effects upon the density caused by heating the upper portion of the tube containing a homogeneous system of ethylene.

Apparatus

The apparatus employed consisted of a single tube of Pyrex glass containing a McBain-Bakr spiral and float for density measurements. The temperature gradient that was used to compress the medium in the lower part of the tube was produced by passing water at a known temperature through a glass jacket that was fitted over the upper section of the bomb. A diagrammatic representation of this assembly is given in Fig. 1.

In order to ensure that the experimental arrangement could not be responsible for the persistent heterogeneity that was developed by the compression, various precautions were taken and must be described fully to demonstrate the reality of the phenomena reported below.

The jacket was made water-tight against the bomb walls by means of a rubber gasket. Two leads were provided in the glass jacket itself to allow a

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circulation of water through it. Two streams of water, one from a hot and the other from a cold water tap, were passed through a mixing chamber, and the temperature of the water issuing from this chamber was read on a thermometer. This water could then be passed through the jacket on the bomb, and the temperature of the return stream was read from a second thermometer placed suitably in the return line. As it was not required that the control and production of temperature be precise, the temperature of the water passing through the jacket was assumed to be the mean of the temperatures of the input and output streams.

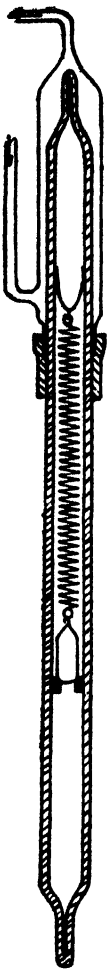
FIG. 1. *Apparatus.*

After the bomb had been filled with ethylene and the top sealed off, the water jacket was affixed in position, and the whole jacket and a large section of the leads were immersed in the thermostat water. Thus, when no passage of water was permitted through the jacket, the temperature of the whole length of the bomb was equal to the temperature of the thermostat. When water was passed through the jacket, a temperature gradient could be maintained along the bomb. It was necessary to ensure that the jacket temperature could return to the precise temperature of the thermostat. The only source of error was likely to be the heat that could be conducted through the leads of the water jacket, which were exposed to the higher temperature of the room. A calculation of the maximum temperature gradient that could be maintained in this way showed a possible value of 0 0008° C. This is less than the fluctuations of the thermostat itself and should not be important. However, to prevent the possibility of such conduction, small copper coils were placed in the bath, in series with the jacket leads. The importance of this precaution is brought out more clearly in the subsequent discussion of the compressional experiments.

Two samples of pure ethylene were used. The source and methods of purification, and also the procedure used in filling the bomb, have already been described (2). One sample of an air-ethylene mixture was studied, and its behaviour compared with that of pure ethylene. The air-ethylene sample was obtained by immersing the bomb containing a pure sample of ethylene in liquid air, cutting off the tip of the capillary, and admitting air directly to the bomb. The tip was then again sealed off. This sample had an unknown air content, estimated at approximately 1.5%, and exhibited the same characteristics as the ethylene–dry-air samples previously studied (3).

Experimental Procedure

The technique of thermostatic control and density determination has been previously described (2, 3). The procedure with these experiments was as follows. With the pure ethylene a complete density-temperature curve was taken in each case before the heating jacket was attached. The results were in agreement with those already obtained with similar systems (2, 3), and are shown in Figs. 2 and 3. These curves were used as reference curves to which

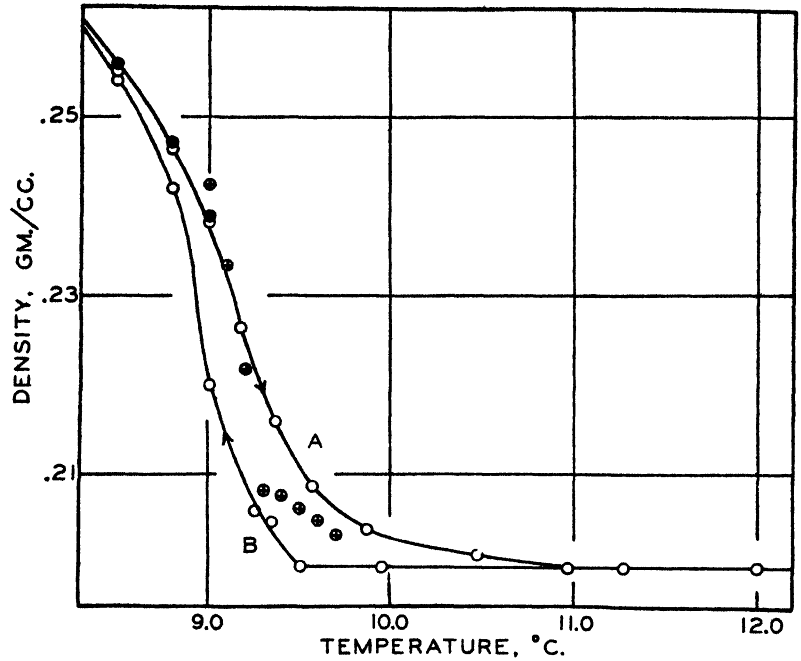

FIG. 2. *Crossed circles denote density after compression with jacket. Solid circles denote density after compression without jacket.*

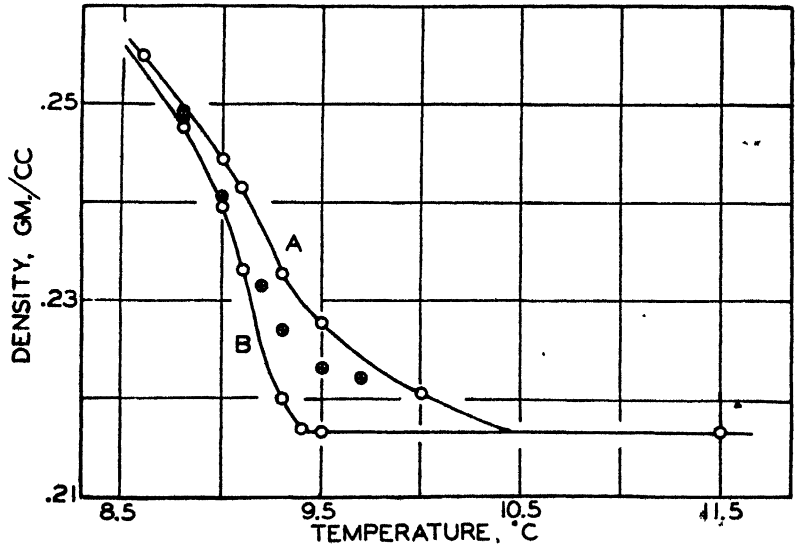

FIG. 3. *Crossed circles denote density after compression with jacket. Solid circles denote density after compression without jacket.*

the densities obtained subsequent to various manipulations were related. With the air-ethylene mixture similar preliminary measurements were made. The value of the mean density was obtained by "molecular stirring", the necessity and significance of which have been discussed elsewhere (3). The results are shown in Fig. 4.

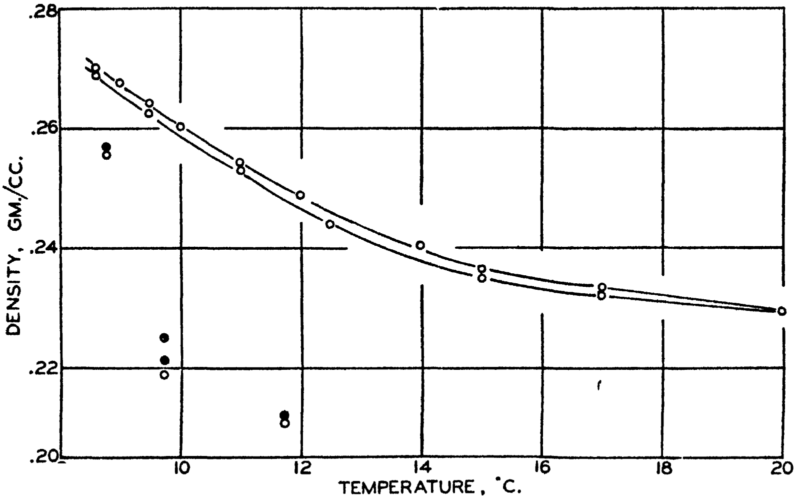

FIG. 4. *Plain circles denote density subsequent to "molecular stirring". Crossed circles denote density subsequent to "molecular stirring" and compression.*

Two methods of compression were used. By lowering the thermostat the upper portion of the bomb was allowed to project outside the bath; it was thus subjected to room temperature, which was some 15° higher than that of the bath. After the desired compression time the thermostat was raised and a time-density curve taken. The second method was compression by means of the heating jacket already described. The duration and extent of heating were varied as desired.

To determine the effect of compression at any given temperature the following procedure was used. The bomb was first heated to 11.5° C. and maintained at this temperature until the average density of the system was attained. The thermostat was then cooled to the desired temperature. When temperature equilibrium was reached, the density value would be represented by a point on curve *B* in the figures. Compression was then carried out by either of the above methods. After compression was removed, a time-density curve was taken until a constant density value was obtained.

The heating jacket and contained water had an insulating effect. Thus, during cooling from 11.5° to the desired temperature, the top of the bomb was always at a higher temperature than the lower part; this produced a slight compressional effect before the main compression was carried out. For the same reason, after the top of the bomb had been heated, the rate of re-establishment of uniform temperature was slower than when no jacket was used.

It is important to note that at no time after heating to 11.5° was any part of the bomb at a temperature lower than that of the thermostat, hence no condensation could occur.

Results

The results of the compressional experiments on ethylene are listed in tables below. The data have been presented in three sections. The first deals with the results obtained when the substance was maintained at a higher temperature than the classical critical of 9.50° C.; the second, with those results obtained between 9.50° and 9.20° C.; and the third group with those at temperatures of 9.17° C. or lower. The reason for this classification is that at 9.17° C. spontaneous condensation occurs, and a liquid phase is formed that possesses a density, as measured in this manner, different from that of the original liquid at the same temperature (2, 3). There are thus seen to be three broad conditions of the systems: the first being at temperatures above the last visual heterogeneity; the second at temperatures lower than this, but above the temperature of spontaneous condensation; and third, at temperatures below that at which the meniscus reappeared.

Table I contains the reference measurements made without the heating jacket in place.

TABLE I

DENSITY-TEMPERATURE REFERENCE CURVE

Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.
Part I. Mean density, 0.1994 gm./cc.					
8.00	0.2658	9.57	0.2085	9.95	0.1994
8.50	.2554	9.87	.2036	9.50	.1994
9.00	.2385	10.47	.2010	9.40	.1997
9.17	.2263	10.97	.1994	8.50	.2543
9.37	.2158	11.27	.1994		
Part II. Mean density, 0.2166 gm./cc.					
8.00	0.2665	9.30	0.2327	9.40	0.2169
8.60	.2554	9.50	.2277	9.30	.2200
8.80	.2495	10.00	.2206	9.10	.2331
9.00	.2445	11.50	.2166	9.00	.2395
9.10	.2416	9.50	.2166	9.80	.2476

Table II contains the compressional data obtained with both samples above the critical temperature. The measurements designated *T* refer to compression with the jacket in position. The other measurements were made by exposing the upper part of the bomb to the air of the room. Times of compression are also recorded in the same tables.

TABLE II

SUMMARY OF RESULTS OF COMPRESSION ABOVE THE CRITICAL TEMPERATURE

Temp., °C.	Density, gm./cc.	Duration of compression, min.	Temp., °C.	Density, gm./cc.	Duration of compression, min.	Temp., °C.	Density, gm./cc.	Duration of compression, min.
Part I. Average density, 0.1994 gm./cc.						*Part II. Average density, 0.2166 gm./cc.*		
9.50	0.2060	— T	9.60	0.2048	5 T	9.70	0.2220	7 T
9.50	.2060	30 T	9.60	.2048	5 T	9.50	.2230	7 T
9.50	.2060	5 T	9.70	.2030	— T			
9.50	.1994	30 –	9.70	.1994	10 –			

TABLE III

SUMMARY OF RESULTS OF COMPRESSION BELOW THE CRITICAL TEMPERATURE AND ABOVE TEMPERATURE OF REAPPEARANCE OF MENISCUS

Temp., °C.	Density, gm./cc.	Duration of compression, min.	Temp., °C.	Density, gm./cc.	Duration of compression, min.
Part I. Average density, 0 1994 gm./cc.			*Part II. Average density, 0.2166 gm./cc.*		
9.40	0.2074	10 T	9.30	0.2270	10 T
9.30	.2081	10 T	9.20*	.2314	10 T
9.20*	.2217	10 T			

Meniscus re-forms, subsequent to compression.

The results obtained below 9.17° C. are given in Table IV. The symbol *T* has the same significance as before.

TABLE IV

SUMMARY OF RESULTS OF COMPRESSION BELOW THE TEMPERATURE OF MENISCUS REAPPEARANCE

Part I. Compressional experiments

Temp., °C.	Density, gm./cc.	Duration of compression, min.	Temp., °C.	Density, gm./cc.	Duration of compression, min.
Mean density, 0.1994 gm./cc.			*Mean density, 0.2166 gm./cc.*		
9.10	0.2335	5 T	9.00	0.2406	— T
9.10	.2335	— T	8.80	.2492	— T
9.00	.2426	— T	8.80	.2486	— —
9.00	.2391	— —			
8.80	.2472	— —			
8.50	.2564	— —			

TABLE IV—*Continued*

SUMMARY OF RESULTS OF COMPRESSION BELOW THE TEMPERATURE OF MENISCUS REAPPEARANCE

Part II. Compressional experiments

Temp., °C.	Density after compression	Density curve *A*	Density curve *B*	Meniscus curve *A*	Meniscus curve *B*	Meniscus after compression
Mean density, 0.1994 gm./cc.						
8.50	0.2564	0.2554	0.2543	20.8	20.3	20.8
8.80	.2472	.2466	—	21.1	19.7	20.8
9.00	.2426	.2385	—	21.3	18.9	20.7
9.10	.2335	.2330	—	21.4	18.0	20.7
Mean density, 0.2166 gm./cc.						
8.80	0.2486	0.2495	0.2476	—	26.3	27.0

These results are represented graphically in Figs. 2 and 3.

From these experiments it is apparent that:—

(1) Above the critical temperature, compression of a homogeneous system re-creates heterogeneity;

(2) Below the temperature of reappearance of the meniscus, the liquid which appears on condensation is increased both in density and amount by the compression;

(3) Just above the temperature of reappearance of a meniscus, i.e., 0.03° C. above, condensation is brought about, and a liquid separates subsequent to compression;

(4) The rate of re-establishment of uniform temperature along the length of the bomb, after application of the pressure gradient, determines the amount of density increase; that is, above the critical temperature, heterogeneity persists only after a slow removal of the pressure gradient, while below the temperature of reappearance, the amount of the density increase is enlarged by slow return to uniform conditions.

(5) The amount of heterogeneity which is re-formed on compression appears to be independent of the magnitude of the temperature gradient, and the length of time during which it is applied.

(6) The branching of the density-temperature curves for various mass-volume ratios occurs for mean densities below 0.200 gm. per cc. at some temperature below 9.00° C.; for this reason compression of the first sample (mean density, 0.1994 gm. per cc.) could create a liquid of a higher density than that of the original liquid. This could not be done with the sample of higher mean density (0.2166 gm. per cc.).

(7) The experiments were reproducible.

(8) The stability of the re-formed heterogeneity was established by following the time-density curves for extended periods after a constant density value was obtained, in one case for an hour and three-quarters beyond the time required for equilibrium. This is a contradiction to the results of experiments performed by F. B. Young (6), who obtained a heterogeneous system in this manner, but who reports its disappearance after removal of the temperature gradient. The reason for this statement is believed to be the lack of sensitivity in the manner of detecting heterogeneous systems. These were recognized by the effect of the refraction of light upon the shape of the lines upon a squared piece of paper. No persistent heterogeneity after compression was found by this method.

The data for the reference curve of the air-ethylene mixture (Fig. 4) are shown in Table V and the results of compression in Table VI. Heterogeneity was re-created by compression in the same manner as with the pure ethylene system. One difference is to be noted—the duration of compression determined the degree of heterogeneity produced, the density difference becoming greater with longer compression. No such effect was observed with pure ethylene.

TABLE V

Air-ethylene mixture

Density-temperature relation after standing at −78° C. for 12 hr. or longer

Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.
8 60	0 2703	14.00	0.2405	11 00	0.2530
9 00	.2678	17 00	2338	9 50	.2629
9 50	.2644	20 00	.2294	8 60	.2695
10.00	2604	17 00	.2324	8 00	.2767
11 00	.2543	15 00	.2365		
12.00	.2492	12 50	.2442		

TABLE VI

Compression of air-ethylene mixture

Mean density, 0.2108 gm./cc.

Temp., °C.	Density before compression	Density after compression
9.50	0.2189	0.2214,10 min.
8.80	.2557	.2570,10
9.50	.2189	.2254,60
12.00	.2108	.2121,10

It is interesting to note that, while determining the original density-temperature curve for the air-ethylene mixture, in one instance the system was heated to 34.5° C., i.e. 25° above the critical temperature. Even at this high temperature the liquid state was not entirely destroyed, as shown from the density and by the nature of the cooling curve which followed back along the heating curve, as with all air-ethylene mixtures, when the heterogeneity is not destroyed (3).

Discussion

Ethylene

The interpretation of these results is based on a new concept of the changes that occur in the transition range of liquid to gas, and which has been derived jointly from the work of the present authors and from that of Naldrett, Mason, and Maass (6). Part of the idea around which this concept grew is discussed in a recent preliminary publication by the authors on the pressure-volume-temperature relations of ethylene in this region. The particular statement is: "apparently, then, the flat portion of the cooling curve of a typical isochore cannot be regarded as representing a homogeneous gas system with the liquid structure destroyed, for such a gas system would not have a pressure independent of the volume over quite appreciable ranges. It is concluded, therefore, that the system, although macroscopically homogeneous, is still a two-phase system, with the effect of the temperature being to disperse or mix mechanically, the two phases".

Since the appearance of the above statement, further work upon the pressure-volume-temperature relations of ethylene has been completed by the authors and will be published shortly. The ideas derived from this work have received strong confirmation through the results of Naldrett, Mason, and Maass, which will also be published shortly. The concept that is presented in these papers is essential to a reasonable explanation of the above-mentioned results, and the salient features which are necessary at the moment, will be anticipated.

It is now believed that above the temperature of 9.20° C. the liquid and vapour phases become miscible in all proportions. Between certain well defined density limits above this temperature, an apparently homogeneous system is in reality heterogeneous, with liquid and vapour phases of densities characteristic for any temperature dispersed completely one with the other, to form a macroscopically homogeneous system. Above 9.90° C. the system acts as a one-phase system, regardless of its mass-volume ratio. The cooling curve, or curve *B*, of a typical isochore, is therefore pictured as a two-phase system of liquid dispersed in vapour. With this background the following explanation of the above results seems quite natural.

In regard to the data of the first division, two distinct features are at once apparent. Compression by means of the water jacket causes a re-forming of a heterogeneous system, while compression with the top exposed does not. The explanation would seem to be as follows. Under the conditions of very great density caused by the compression, the amount of liquid is altered to that amount which is characteristic of the greater mass-volume ratio, and this tends to settle to the bottom of the tube. If the subsequent expansion is slow, the liquid is not entirely redistributed, and a heterogeneity persists. On rapid expansion the heterogeneity is again destroyed.

As the temperature is lowered below 9.50° C., conditions suitable to the spontaneous stratification of liquid are more nearly approached. At 9.20° C., conditions are such that compression can cause a large enough number of liquid molecules to group together for settling out to be possible, and condensation occurs.

The liquid that condenses out at 9.17° C. is of a nature different from that of the visible liquid that is shown by the original heating curve to be present at 9.17° C., if the density measurement is truly of the liquid phase alone. Compression changes the characteristic density and the amount of liquid, as Table IV shows. The change is assumed to be caused in the following manner. The dispersion of vapour in liquid, which has been brought about by heating and then cooling, is altered on compression. The compression largely changes the vapour groups in the liquid to liquid groups. In addition, liquid that is still dispersed in the vapour drains out, and both the density and the amount of the liquid is increased.

Moreover, the lower density of the liquid phase at 9.00° C. on heating up for the filling of mean density 0.1994 gm. per cc., compared to the constancy of liquid density at this temperature for fillings of higher average density (3), is explained by the greater amount of vapour in the liquid phase. Compression of the re-formed liquid at this low average density at 9.00° C. on the curve *B* causes an increase in density above that of the original heating curve, but never in excess of the density of 0.245 gm. per cc. which is characteristic for the fillings of higher mean density. This can be explained on the assumption that, at the low mean density under discussion, the mechanism of compression does not permit as great an artificial density to be developed, and some of the vapour is left unchanged in the liquid, with a consequent lower liquid density even after compression.

Air-Ethylene System

Although a mechanism for the behaviour of pure ethylene, when compressed as described above, has been offered, it does not seem feasible in the present state of our knowledge of multi-component systems to extend the same explanation to an air-ethylene mixture. The real interest in the study of such systems has been with respect to the hypotheses of earlier workers (5, 6); who have attempted to explain the anomalous behaviour in the critical region by the presence of minute quantities of impurities.

It was pointed out in an earlier paper (3) that small quantities of air contained in an ethylene sample increased the amount of heterogeneity and the temperature range above the classical critical temperature throughout which the liquid phase may persist. In the present study it is apparent that the presence of air now retards the establishment of a heterogeneous system from a homogeneous one, and impurities of such a nature would tend to obscure the phenomena caused by compression. The reason for this behaviour cannot be discussed upon any firm basis until the effect of the impurity upon the interfacial tension has been established.

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PRESSURE, VOLUME, TEMPERATURE RELATIONS OF ETHYLENE IN THE CRITICAL REGION. II[1].

By R. L. McIntosh[2], J. R. Dacey[2], and O. Maass[3]

Abstract

The data of a previous publication have been extended. Nine pressure isothermals of the one component system ethylene in the critical region are given. Further evidence of the existence of a two phase system above the temperature of meniscus disappearance as normally determined is presented. The existence of a latent heat of vaporization above this temperature is pointed out. An explanation of the hysteresis of liquid phase density with temperature at constant volume is offered, and a qualitative description of the changes occurring in the transition region of liquid to gas is developed from the experimental evidence.

Introduction

In an earlier paper the authors reported the determination of isothermals of ethylene from 8.92° to 9.60° C. (2). Unfortunately, an explosion destroyed the apparatus before all the desired data had been obtained. The present paper describes the continuation of these experiments.

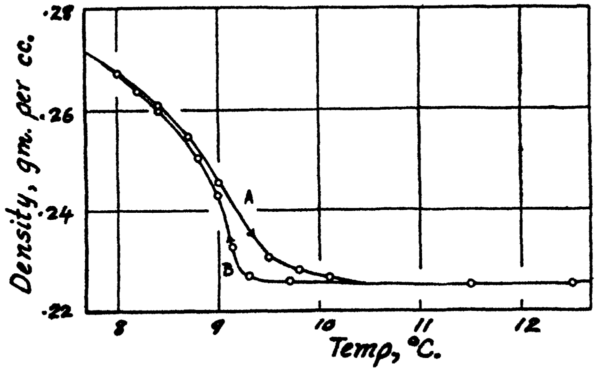

Fig. 1. *Isochore. A. Densities of medium below meniscus on heating above critical temperature. B. Densities subsequently observed during cooling.*

The interest in the work centres about the pressure relations that exist along the *A* and *B* curves of a typical isochore (Fig. 1). It was found by Maass and Geddes that the pressures of the *A* and *B* curves were identical at any given temperature for the average density investigated by them (5). Also, the pressure of a heterogeneous system was shown to be the same as that of a homogeneous system at the same average density, obtained by isothermal expansion from liquid densities. The isothermals obtained by Maass and Geddes failed to exhibit any region of density wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$, above the classical critical temperature. The prediction of Harrison and Mayer that such regions should exist, even above the critical temperature, was therefore not corroborated (4). A pertinent criticism by Mayer of this experimental work, in which he pointed out that observations had not been taken at sufficiently minute volume intervals, has led to the construction of an apparatus with which pressure, volume, temperature measurements of a high relative accuracy can be made. For a description of this type of apparatus, and an account of the preliminary measurements made with it, the reader is referred to the earlier paper (2). Added weight was given to Mayer's observation by the work of McIntosh and Maass, which showed that the pressure of heterogeneous systems at 9.80° C. was independent of the mass-volume ratio over an appreciable range of density (6). If the earlier work were to be concordant with this, the isothermals must necessarily exhibit regions even above the critical temperature, where $\left(\frac{\partial P}{\partial V}\right)_T = 0$. That such regions are detectable has been shown in the preliminary publication. In the present work the envelope of these regions has been completely traced, and the pressure relations that hold within it have been investigated.

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Contribution from the Division of Physical Chemistry, McGill University, Montreal, Canada, with financial assistance from the National Research Council of Canada.

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Experimental Results

Nine isothermals from 8.92° to 10.00° C. are given in Table I, and are shown in Fig. 2. The previously published figures are included and the whole

TABLE I

Pressure-volume-temperature relations of ethylene

Exp. vol.	Amount of ethylene, gm.	Specific vol.	Press., atm.	Exp. vol.	Amount of ethylene, gm.	Specific vol.	Press., atm.
Isothermal at 8.92° C.							
2.532 2 587 2.672 2.893	0.716 .716 .716 .716	3.563 3 613 3 731 4.040	49.92 49.73 49.54 49.45	3.271 3 681 4.303 4.317	0.716 .716 .716 .716	4.568 5.141 6.009 6.029	49.45 49.46 49.38 49.34
Isothermal at 9.22° C.							
2.590 2 613 2.655 2.715 2.794 2.830	0.716 .716 .716 .716 .716 .716	3.617 3.649 3.708 3.791 3.902 3.952	50.18 50.06 49.96 49.87 49.83 49.80	2.970 3.284 3.666 3.876 4.006 4.174	0.716 .716 .716 .716 .716 .716	4.148 4.586 5.120 5.410 5.594 5.831	49.75 49.75 49.73 49.72 49.68 49.65

TABLE I—*Continued*

PRESSURE-VOLUME-TEMPERATURE RELATIONS OF ETHYLENE—*Continued*

Exp. vol.	Amount of ethylene, gm.	Specific vol.	Press., atm.	Exp. vol.	Amount of ethylene, gm.	Specific vol.	Press., atm.
Isothermal at 9.42° C.							
2.710	0.716	3.770	50.26	3.300	0.716	4.609	49.99
2.735	.716	3.819	50.15	3.550	.716	4.958	49.97
2.838	.716	3.963	50.06	3.723	.716	5.199	49.94
2.950	.716	4.120	50.02	3.910	.716	5.446	49.90
3.176	.716	4.437	49.99	4.104	.716	5.731	49.85
Isothermal at 9.50° C.							
2.705	0.716	3.777	50.44	2.970	0.716	4.148	50.12
2.722	.716	3.801	50.34	3.235	.716	4.519	50.08
2.762	.716	3.857	50.24	3.455	.716	4.826	50.07
2.789	.716	3.895	50.21	3.624	.716	5.061	50.05
2.829	.716	3.951	50.19	3.857	.716	5.386	49.98
2.908	.716	4.047	50.14	4.197	.716	5.861	49.92
Isothermal at 9.60° C.							
2.695	0.716	3.763	50.52	3.512	0.716	4.891	50.15
2.713	.716	3.775	50.45	3.607	.716	5.037	50.14
2.756	.716	3.849	50.34	3.710	.716	5.181	50.13
2.854	.716	3.986	50.27	3.859	.716	5.389	50.09
3.135	.716	4.378	50.18	4.020	.716	5.614	50.05
3.360	.716	4.692	50.17				
Isothermal at 9.70° C.							
2.823	0.722	3.909	50.42	3.318	0.722	4.605	50.27
2.884	.722	3.994	50.35	3.414	.722	4.729	50.25
2.953	.722	4.090	50.30	3.640	.722	5.041	50.22
3.109	.722	4.306	50.28	3.885	.722	5.381	50.18
3.187	.722	4.414	50.28	4.004	.722	5.546	50.17
Isothermal at 9.80° C.							
2.761	0.722	3.824	50.65	3.066	0.722	4.246	50.40
2.776	.722	3.844	50.61	3.108	.722	4.304	50.39
2.808	.722	3.889	50.56	3.197	.722	4.429	50.39
2.863	.722	3.965	50.50	3.262	.722	4.518	50.38
2.902	.722	4.019	50.47	3.328	.722	4.609	50.37
2.954	.722	4.091	50.44	3.464	.722	4.792	50.34
3.025	.722	4.189	50.42	3.635	.722	5.030	50.32
Isothermal at 9.90° C.							
2.770	0.722	3.837	50.74	3.072	0.722	4.255	50.52
2.807	.722	3.890	50.69	3.132	.722	4.338	50.51
2.854	.722	3.953	50.65	3.224	.722	4.466	50.50
2.923	.722	4.048	50.60	3.302	.722	4.574	50.48
2.961	.722	4.101	50.57	3.512	.722	4.864	50.45
3.030	722	4.197	50.54	3.737	.722	5.178	50.42

TABLE I—*Concluded*

PRESSURE-VOLUME-TEMPERATURE RELATIONS OF ETHYLENE—*Concluded*

Exp. vol.	Amount of ethylene, gm.	Specific vol.	Press., atm.	Exp. vol.	Amount of ethylene, gm.	Specific vol.	Press., atm.
Isothermal at 10.00° C.							
2.820	0.722	3.905	50.79	3.155	0.722	4.370	50.63
2.913	.722	4.034	50.72	3.236	.722	4.482	50.61
3.005	.722	4.162	50.67	3.396	.722	4.703	50.57
3.045	.722	4.217	50.66	3.750	.722	5.194	50.51
3.083	.722	4.270	50.64				

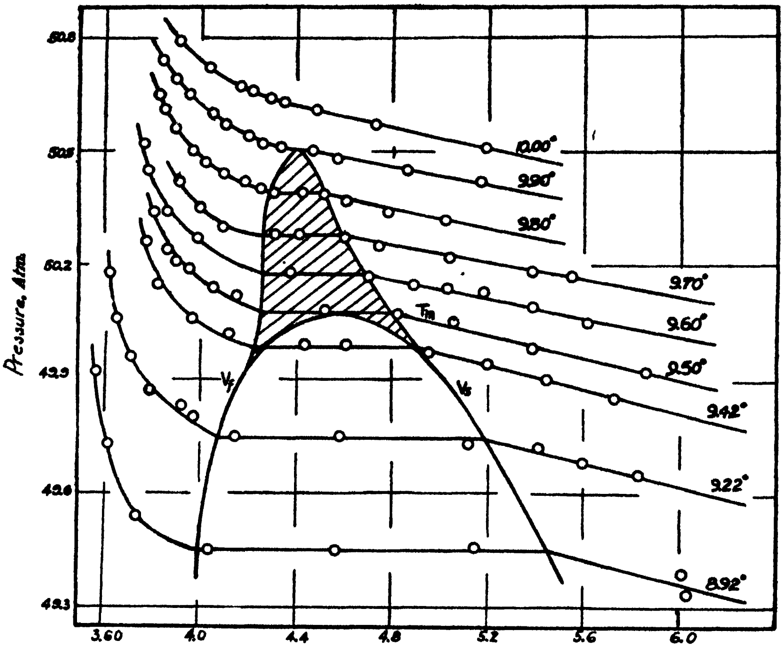

FIG. 2. *Isothermals. Relation between specific volume and pressure at temperatures in the critical temperature region.*

tabulated in terms of specific volume. The experimental error in determining the absolute densities is ±1%. In order to show that the contiguity of the curves obtained with the two assemblies used is real, the isothermal at 9.22° C. was repeated. The agreement was exact.

Pressure measurements along the *A* and *B* curves of isochores of three different mean densities were made, in order to determine the relative stabilities of the heterogeneous and homogeneous systems under a variety of conditions. These results are shown in Table II.

TABLE II

PRESSURE MEASUREMENTS OF HETEROGENEOUS SYSTEMS

Temp., °C.	Pressure, atm. density = 0.2046 gm./cc.	Pressure, atm. density = 0.2109 gm./cc.	Pressure, atm. density = 0.2270 gm./cc.	Pressure of isothermals
Heating				
9.00	49.50	49.51	49.50	
9.20	49.74	49.75	49.74	49.74
9.50	50.06	50.07	50.06	50.07
9.80	50.38	50.39	50.40	50.39
10.50	51.13	51.15	51.22	Limit of flat portion of isothermal corresponding to limit of $\left(\frac{\partial P}{\partial V}\right)_T = 0$ at 10.00°.
11.00	51.66	51.69	51.84	
Cooling				
10.50	51.12	51.15	51.22	
9.80		50.39	50.40	
9.50	50.06	50.07	50.06	
9.20	49.74	49.75	49.74	
9.00	49.50	49.51	49.50	

Discussion

The interpretation of these results is based on the assumption that the isothermals obtained by expansion from liquid densities are equilibrium curves and represent stable states of the system. It is now realized that adequate proof of this is lacking. However, the evidence obtained directly upon this point and published previously (2), together with all subsequent data, indicates that such is the case.

The experimental results show clearly that:

(1) Pressure isothermals above and below the temperature of meniscus disappearance contain regions of density wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$. This region can no longer be observed on the isothermal at 10.00° C.

(2) The complete envelope of this region has been determined.

(3) The pressure of a heterogeneous system whose mean density is represented by a point within this envelope is the same as the pressure corresponding to the horizontal portion of the macroscopically homogeneous isothermal. The pressure of such heterogeneous systems is independent of the mass-volume ratio within such density limits.

(4) The pressure of heterogeneous systems corresponds exactly to the pressure of homogeneous systems obtained by heating at constant volume to 10.50° C. or higher, and cooling to the temperature at which the pressure of the heterogeneous system was measured, so long as the mean density of the system is within the envelope of the horizontal regions.

(5) A discrepancy between the value of the pressure at 9.50° C. obtained by Maass and Geddes (5) and that by the authors is apparent. The pressure-

temperature curves of the former workers varied above 9.2° with mass-volume ratio. This result has not been duplicated. Indeed, the pressure-temperature values here given are independent of mass-volume ratio, provided that the mean density of the system lies within the region where $\left(\frac{\partial P}{\partial V}\right)_T = 0$.

(6) The pressure-temperature curves at constant volume are reversible.

Corroboration of Prediction by Mayer and Harrison

Harrison and Mayer, as already pointed out, have made calculations of particular interest as to the possible behaviour of a one component system in the critical-temperature–critical-pressure region (4). The theoretically predicted diagram given by these authors shows a startling similarity to that of the experimentally determined isothermals represented in Fig. 2. The continued existence of regions wherein $\left(\frac{\partial P}{\partial V}\right)_T = 0$ above the temperature of meniscus disappearance is completely verified by experiment. The suggested symmetry of this region about V_c is, however, not apparent. The experimental isotherms show a nearly perpendicular boundary for V_f, while V_s slopes noticeably toward the higher densities as the temperature is raised. V_s, V_f, and T_m have the same significance as in the nomenclature of Harrison and Mayer.

Explanation of Liquid Density Hysteresis Curve

From the above data it is apparent that a two phase system of liquid and vapour continues to exist above T_m, the temperature of meniscus disappearance. The two phases may or may not form an apparent homogeneous system, depending on the thermal treatment and mechanical stirring to which it has been subjected. The dispersion of one phase in the other is apparently possible because of a zero or very minute surface tension (9, 11). The value of the surface tension explains the equivalence of pressures of heterogeneous and homogeneous systems. With this hypothesis as the basis, a reasonable explanation for the density hysteresis of the liquid phase as measured by the spiral and float method may now be offered.

On heating a two phase system at constant volume from well below the critical temperature, the density of the liquid phase rapidly diminishes as the classical critical temperature is approached. A heterogeneous system continues to exist until the temperature is slightly above 10.00° C., where a homogeneous medium is formed. This system would be represented by a point somewhere above the shaded area of Fig. 2. It exhibits the behaviour of a one phase system. On cooling from this temperature, liquid re-forms and is distributed evenly throughout the tube, as the unchanging density value shows. As the temperature decreases, the interfacial tension between the phases increases, until at 9.20° C. it is sufficiently great for spontaneous stratification to occur, and a liquid phase is seen to separate. The apparent density of this liquid does not coincide with the liquid density on the original heating curve until a temperature of 8° C. has been reached (See Fig. 1).

This is believed to be caused by a residual quantity of vapour remaining suspended in the liquid. The amount of vapour that the liquid can retain decreases with decreasing temperature, until at 8° C. it is so small that the true liquid phase density is again exhibited. This concept has been incorporated in a previous paper to explain the effect of compression on the density and on the amount of the liquid that separates at 9.20° C. (9, 11). The fact that the phase densities at the classical critical temperature are a function of the mass-volume ratio (6) can also be explained by a mutual dispersion of the two phases. Further evidence supporting this hypothesis will be published shortly by Naldrett, Mason, and Maass (8).

Critical Constants as Determined from the Pressure-volume Isothermals

From the envelope of the region for which $\left(\frac{\partial P}{\partial V}\right)_T = 0$ the true critical constants of ethylene may be determined. The point of inflection, $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$, gives that temperature at which liquid can no longer exist under its own vapour pressure. The pressure, temperature, and specific volume of this point are respectively, 50.50 atm., 9.90° C., and 4.40 cc.

Vapour Pressure of Ethylene between 8.92° and 9.90° C.

The isothermals given above have been used to determine the vapour pressure curve of ethylene in the critical region. The values are given in Table III, and are represented in Fig. 3. The pressure for any one temper-

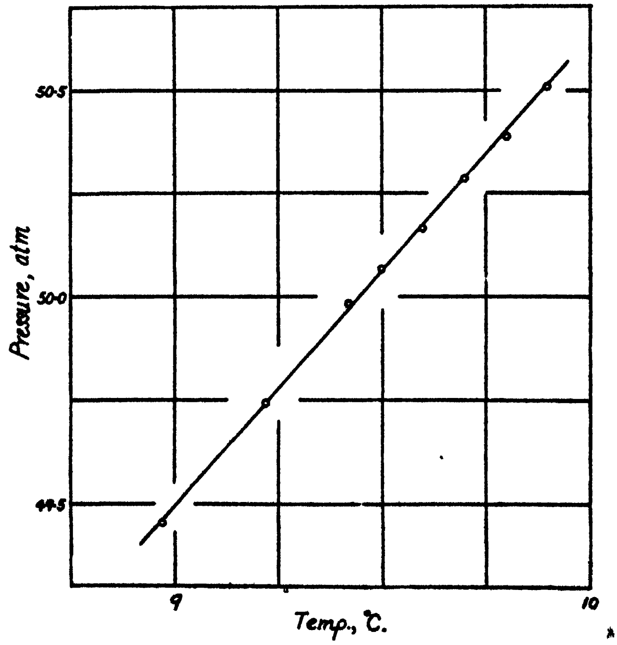

FIG. 3. *Relation between vapour pressure and temperature in the critical temperature region.*

TABLE III

VAPOUR PRESSURE OF ETHYLENE

Temp., °C.	8.92	9.22	9.42	9.50	9.60	9.70	9.80	9.90
Av. press., atm.	49.45_3	49.74_3	49.98_3	50.06_6	50.16_6	50.27_6	50.38_6	50.51_0

$$\text{From Fig. 3.}\quad \frac{\partial P}{\partial T} = \frac{50.600 - 49.450}{9.975 - 8.960}\ \text{atm./°C.}$$

$$\frac{1.150}{1.015}\ \text{atm./°C.} = 1.13_3\ \text{atm./°C.}$$

ature was taken as the average of the pressures determined in the region for which $\left(\frac{\partial P}{\partial V}\right)_T = 0$. Although pressures are given in Table I to 0.01 atm. only, the average should be somewhat better, and the last figures in Table III have been included for this reason. As is to be expected over such a narrow range of temperature, the vapour pressure as a function of temperature is excellently represented by a straight line.

Heat of Vaporization in the Critical Region

The latent heat of vaporization may be calculated from the Clausius-Clapeyron equation,

$$T\,\frac{\alpha P}{\alpha T} = \frac{\lambda}{V_2 - V_1}$$

where λ is the latent heat of vaporization in cal. per gm.;

V_2 is the specific volume of the saturated vapour;

V_1 is the specific volume of the saturated liquid.

The value of $\frac{\alpha P}{\alpha T}$ was evaluated graphically from the figures of Table III, while the specific volumes of vapour and liquid were determined from the saturation curve of Fig. 2. These values are tabulated in Table IV, and the latent heat as a function of temperature is represented in Fig. 4. A latent heat is seen to exist at 9.50° C., which is the classical critical temperature.

TABLE IV

V_2	V_1	T	$\frac{\alpha P}{\alpha T}$	λ cal./gm.	$V_2 - V_1$
5.448	4.000	282.1	1.13	11.19	1.448
5.176	4.072	282.4	1.13	8.53	1.104
4.896	4.224	282.6	1.13	5 20	.672
4.800	4.256	282.7	1.13	4.21	.544
4.688	4.256	282.8	1.13	3.34	.432
4.596	4.256	282.9	1.13	2.63	.340
4.520	4.280	283.0	1.13	1.86	.240
4.400	4.400	283.1	1.13	0	0

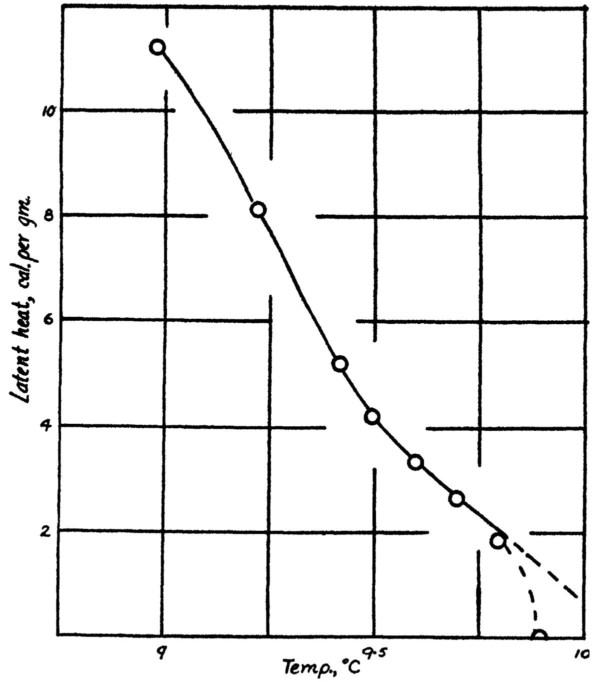

FIG. 4. *Relation between latent heat of vaporization and temperature in the critical temperature region.*

A better value of the temperature at which the point of inflection of the isothermals occurs may be obtained from an extrapolation of the latent-heat–temperature curve. The temperature of 9.90° C. was taken since this is the last isothermal that exhibits a detectable region where $\left(\frac{\partial P}{\partial V}\right)_T = 0$. The sensitivity of the experimental method limits the accuracy of such a choice, and an improvement may be made by extrapolating the smooth curve of latent heat against temperature. Such an extrapolation indicates a temperature of slightly more than 10.00° C., which is in excellent agreement with the temperature of minimum viscosity found by Mason and Maass (7).

Qualitative Description of Transition from Liquid to Gas

In addition to the evidence presented here, which suggests a dispersion basis for part of the process of transition, time lags have been recorded that are very great when a system in the "vapour" region of densities has its conditions changed in such a manner as to cause a shift toward "liquid" densities (5, 6, 8). These time lags have been interpreted as indicative of a change in degree of orientation as the liquid state is approached. From such data the following description of the changes that occur on liquefaction has been developed. It is, in essence, a combination of the ideas proposed by Traube (8), Maass and his co-workers, and Bradley, Browne, and Hale (1).

The distinction made by Traube between real liquid (liquidons) and real gas (gasons), and between the liquid phase and the vapour phase might even even be retained subject to the following interpretations. In that case the liquid phase is to be considered as liquidons containing true gas in solution while the vapour phase contains true liquid in solution in gasons. The difference between a liquidon and a gason may be that a gason is a single molecular unit, or at least is made up of few molecules, whereas a liquidon is a group of gasons. On compression of a mass of gasons, orientation and clustering occur at random throughout the gas, and small groups of liquidons form and break up as the kinetic theory demands. Thus the life of any one group is limited, but such groups are always present. On further compression below the critical temperature the number of groups increases until saturation has been attained, and precipitation of the liquid phase occurs. This phase contains a saturation value of gasons. To quote directly from Bradley, Browne and Hale, "This view transforms the area of liquefaction on a diagram of isothermals to an area of saturation. Outside this area, on the side opposite the pressure axis, liquidons may exist, less or more according to volume, but never to the extent of saturating the gasons in which they are dissolved." With regard to gasons in the liquid the opposite is true. "Above the critical temperature, true gas and true liquid may exist side by side in any proportion, according to volume, but there can never be phases except in the loose sense of temporary stratification. Outside the area of saturation there is perfect continuity in every direction. The area of saturation, indeed, is after all only an exceptional case in an otherwise general continuity between the liquid and gaseous conditions of matter."

In the case of ethylene, below 9.20° C., the saturated phases of liquid and gas are separated into layers. Between this temperature and the temperature above which the molecular species are infinitely soluble one in the other (10° C., approximately), two saturated phases co-exist, and remain in layers, or are dispersed one in the other, depending upon the treatment to which the system is subjected. Above this temperature a saturation value is impossible and the system acts as a one phase system. At sufficiently small densities it will exhibit the behaviour characteristic of a gas, and at very great densities it will exhibit that of a liquid.

A review will appear of the ideas held at present in this laboratory in regard to the nature of the change of state in the critical-pressure—critical-temperature region.

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THE CONVERSION OF ALPHA-BROMONAPHTHALENE INTO THE BETA ISOMER[1]

By Herbert E. Fisher[2] and R. H. Clark[3]

Abstract

L. Roux found that α-bromonaphthalene was partly converted into β-bromonaphthalene by warming with aluminium chloride and carbon disulphide. Because of the interest in the β-derivatives for the preparation of naphthalene-2-acetic acid, one of the synthetic plant hormones, this investigation was undertaken to improve, if possible, upon the yield hitherto obtained. Several metals, notably antimony, molybdenum, nickel, and tungsten, in conjunction with aluminium chloride, gave increased yields.

Introduction

The conversion of α-bromonaphthalene into the more difficultly synthesized β-compound is of importance for the synthesis of naphthyl-2-acetic acid.

This transformation was first studied by Roux (2), who heated the α-compound with aluminium chloride in a carbon disulphide solution, and reported a yield of 15% of the β-derivative. He postulated the formation of an intermediate compound with aluminium chloride, which in turn decomposed, giving the β-isomer.

Mayer and Schiffner (1) found, by passing α-bromonaphthalene over silica gel in a porcelain tube at 350° C., that a very small quantity of the β-bromonaphthalene was formed. Attempts to make the β-bromo compound from β-naphthol directly have not been very successful (3).

Since any direct method for the preparation of β-bromonaphthalene did not appear to be promising, this investigation was undertaken to see whether the process originally developed by Roux could be modified to give an increased yield. Variations in temperature, solvents, and catalysts were employed.

Experimental

The reaction mixture was in every case placed in a 500 cc. Claisen flask, to one neck of which was attached a reflux condenser, to prevent loss of the volatile solvent; through the other neck passed a motor driven stirrer with a mercury seal. Local overheating was prevented by means of a second stirrer in the water bath.

Several attempts to follow the directions given by Roux gave a maximum yield of 9.1%, calculated on the basis of the α-bromonaphthalene utilized.

Among the modifications then employed was a change of solvent. The carbon disulphide was replaced by such solvents as acetone, benzene, aqueous and absolute alcohol, dioxane, aqueous and anhydrous pyridine, and nitromethane. No conversion whatsoever was obtained with these solvents.

Other catalysts, both to replace and to augment the action of the aluminium chloride, were then investigated. Freshly prepared anhydrous ferric chloride was used in place of the aluminium chloride; no β-compound was obtained, the α-compound being recovered almost quantitatively.

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Contribution from the Department of Chemistry, The University of British Columbia, Vancouver, B.C., Canada.

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Various multi-valent metals were then added in small quantities to the aluminium chloride, in search of a promoter for the reaction. A typical procedure was: 350 cc. of carbon disulphide, 100 gm. of α-bromonaphthalene, 10 gm. of anhydrous powdered aluminium chloride, and 0.5 gm. of nickel were placed in the Claisen flask, fitted with reflux condenser and mercury seal stirrer, and refluxed for one hour at 50° C. Preliminary experiments showed these to be the optimum conditions for the conversion. The contents of the flask were then decanted into cold water, stirred to dissolve any aluminium chloride, and the carbon disulphide layer was filtered to remove the nickel. The solvent was distilled off, after which the temperature was raised, and naphthalene, and a mixture of α- and β-bromonaphthalene, successively collected at temperatures of 220 to 260° C. and 270 to 310° C., respectively. The mixture was chilled to 5° C. in a refrigerator; the solid product was pressed between filter paper, while kept at this temperature, and the β-derivative collected, and recrystallized from 95% alcohol.

Table I gives the results obtained with various metals. The percentage yield is calculated on the basis of the α-bromonaphthalene utilized.

TABLE I

YIELDS OF β-BROMONAPHTHALENE WITH VARIOUS METALS

Promoter	β-bromonaphthalene obtained, gm	α-bromonaphthalene recovered, gm	Naphthalene, gm	Yield, %
Antimony	18.0	20.0	10.5	22.5
Molybdenum	20.0	19.0	13.0	25.0
Selenium	13.0	21.0	11.8	16.0
Nickel	22.0	14.0	14.5	25.5
Tungsten	18.0	13.5	15.0	23.5
Chromium	12.5	13.5	11.5	14.4
No promoter	8.5	7.0	10.5	9.1

Remarks

Carbon disulphide would appear to be the only solvent suitable for the conversion of α-bromonaphthalene into the β-bromonaphthalene. Although it was found that a practically quantitative recovery of the solvent was possible at the end of the heating period, it is not improbable that an intermediate compound is formed with the carbon disulphide.

The mechanism of the action of promoters is still obscure. Since several reactions are taking place simultaneously, such as the production of naphthalene, β-bromonaphthalene, dibromonaphthalene, hexabromonaphthalene, and tar, it is possible that the promoter retards the side reactions, or accelerates the main reaction.

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STARCH CONTENT OF CERTAIN WHEATS OF THE 1935 CROP[1]

By Clarence Yardley Hopkins[2]

Abstract

Average samples of 12 grades of Western Canadian wheat (1935 crop) were analyzed for starch by a polarimetric method. The samples of the ordinary milling grades, in which Marquis was the predominant variety, contained from 50 to 52% of starch on a basis of 13.5% moisture. Samples of Garnet wheat contained about 55% starch. Rusted wheat had a lower starch content. There is positive correlation between starch content and specific gravity of the kernels.

Comparison with data obtained elsewhere on the same samples shows that the sum of the starch and protein is closely related to the flour yield.

Introduction

In connection with a survey of possible industrial uses for Canadian wheat, the starch content of a number of samples of the 1933 crop was determined (4). In that year the grain was of high quality and a very large percentage was graded One and Two Northern.

The 1935 crop was more widely distributed among the various grades. Three special grades were also set up to provide for seriously rusted wheat and two new grades were established for Garnet wheat. Representative samples were therefore obtained from 12 different classifications including the rusted grain and the Garnet variety.

The samples were supplied through the kindness of Dr. W. F. Geddes of the Grain Research Laboratory at Winnipeg. They were taken from the "Winnipeg Averages", which are composite samples representative of the wheat passing through Winnipeg to eastern markets.

Experimental

The grain was cleaned, ground, and analyzed for moisture in accordance with the methods described previously (4). Starch determinations were made by a polarimetric method (3). The analytical results are given in Table I.

The specific gravity of the kernels was determined by the pycnometer method of Bailey and Thomas (1).

A graphical comparison of starch content, specific gravity, and weight per bushel is shown in Fig. 1. The figures for weight per bushel are taken from the annual report of the Grain Research Laboratory (2), as are the data on protein content and flour yield shown in Fig. 2. The determinations were made on the same composite samples that were used in the present investigation.

The correlation between starch content and specific gravity is high ($r = .86$; 1% point $= .71$).

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa. Presented before Section III of the Royal Society of Canada, May, 1936. Issued as N.R.C. No. 835.

Chemist, National Research Laboratories, Ottawa.

TABLE I

Starch content of wheat samples from 1935 crop

Grade of wheat	Moisture, %	Starch, % (as received)	Starch, % (13.5% moisture basis)
1 Hard	8.40	(55.22, 55.39) 55.31	52.23
1 Northern	8.62	(53.55, 53.65) 53.60	50.74
2 Northern	9.57	(54.00, 53.89) 53.95	51.60
3 Northern	8.44	(53.84, 53.91) 53.88	50.90
4 Northern	8.21	(53.09, 53.23) 53.16	50.09
5 Wheat	8.35	(53.25, 53.35) 53.30	50.30
6 Wheat	7.83	(52.02, 52.28) 52.15	48.94
4 Special	7.82	(52.53, 52.66) 52.60	49.35
5 Special	7.26	(51.37, 51.47) 51.42	47.96
6 Special	6.87	(51.45, 51.47) 51.46	47.80
1 C.W. Garnet	7.36	(58.91, 59.21) 59.06	55.14
2 C.W. Garnet	8.05	(58.13, 58.22) 58.18	54.74

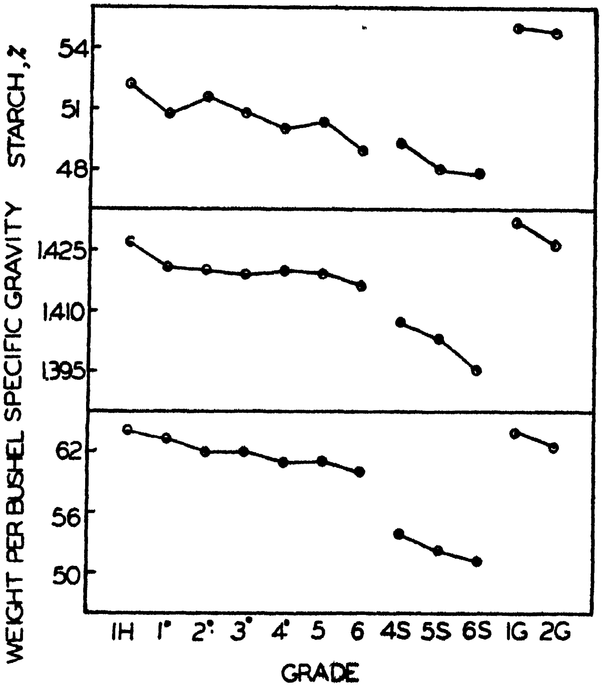

Fig. 1. *Comparison of starch content of wheat with physical properties of the kernels.*

Starch Content and Flour Yield

A comparison of starch content, protein content (2), and flour yield (2) is shown graphically in Fig. 2. Both starch and protein content decline irregularly from the higher to the lower grades. The Garnet samples are characterized by low protein and high starch content.

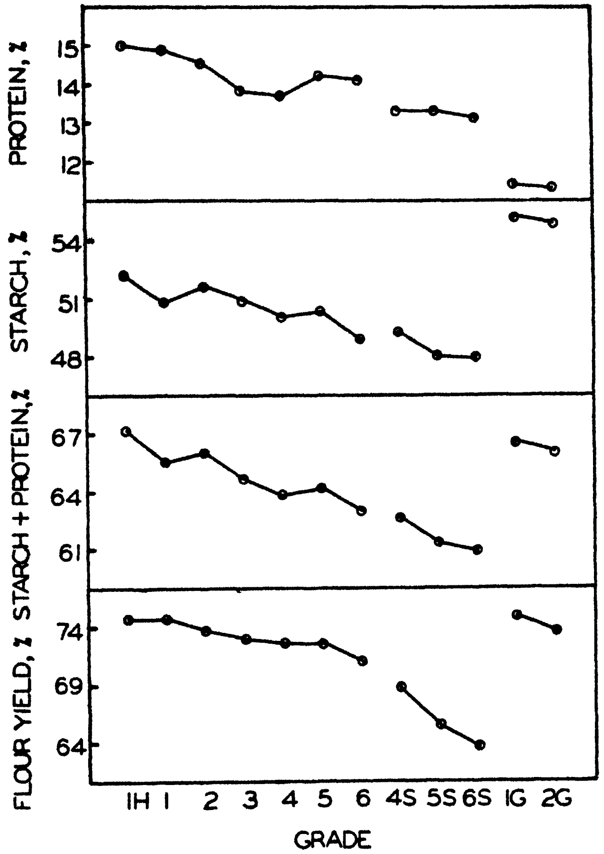

FIG. 2. *Comparison of starch content, protein content, and flour yield of wheat.*

There is a very close relation between the flour yield and the sum of the starch content and protein content in these samples. The relation, however is curved and is given by the equation

$$y = -1269.69 + 40.2504x - .301309x^2.$$

where y = flour yield and x = starch content + protein content (Fig. 3).

This equation fits the data almost exactly, the multiple correlation being $R = .986$. The result of these analyses indicates that it may be possible to predict the flour yield of new varieties of wheat by determining starch and protein content, using a relatively small sample.

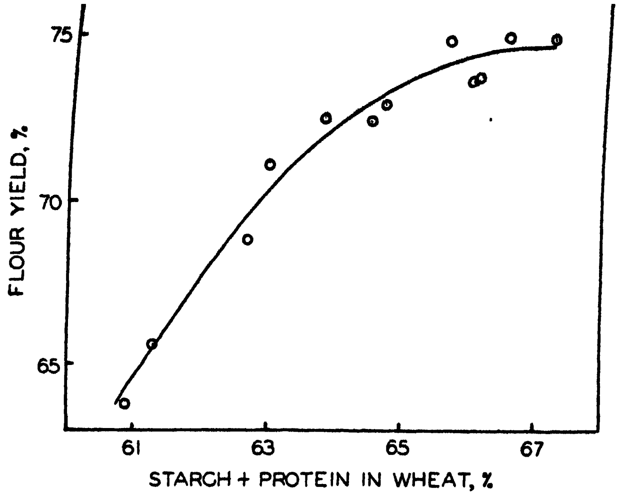

FIG. 3. *Relation between flour yield and starch + protein. The experimental results are plotted along with the curve which represents the mathematical relation between these two variables.*

The protein content of the Garnet grades seems to be unusually low in these crop samples. However, the sum of the starch and protein is practically the same as in the corresponding grades of Marquis wheat (Table II).

TABLE II
MARQUIS AND GARNET SAMPLES
(13.5% moisture basis)

Grade	Starch, %	Protein, % (2)	Starch + protein, %
1 Northern (Marquis)	50.7	14 9	65.6
2 Northern (Marquis)	51.6	14.5	66.1
1 C.W. Garnet	55.1	11.4	66.5
2 C.W. Garnet	54.7	11.3	66.0

TABLE III
COMPARISON OF SAMPLES FROM 1933 AND 1935 CROPS
(13.5% moisture basis)

Grade	Starch, %		Protein, %		Starch + protein, %	
	1933	1935	1933	1935 (2)	1933	1935
1 Northern	51.9	50.7	14.4	14.9	66.3	65 6
2 Northern	52.0	51.6	14 0	14 5	66.0	66.1
3 Northern	50.1	50.9	14.5	13.8	64.6	64.7
4 Northern	51.0	50.1	13.2	13.7	64.3	63.8
5 Wheat	52.0	50.3	12.2	14.2	64.2	64.5
6 Wheat	51.5	48 9	12.8	14.1	64.3	63.0
Mean	51.4	50.4	13.5	14.2	64.9	64.6

Comparison with 1933 Crop Analyses

The previous investigation (4) included analyses of some samples of the 1933 crop from the grades 1 Northern to 6 inclusive. Comparative figures are shown in Table III.

The starch content of the 1935 crop samples is somewhat lower and the protein content somewhat higher than was found in the 1933 samples. The sum of the starch and protein, however, is virtually the same.

The three special grades of the 1935 crop, containing heavily rusted wheat, were shown to be low in protein (2). It had been expected that these grades, made up in large proportion of shrunken kernels, would be low in starch but high in protein owing to the high ratio of bran and germ to endosperm.

Since both starch and protein are lower than in undamaged wheat, it is concluded that the content of fibre and hemicelluloses must be correspondingly higher.

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2 : 2′-BIQUINOLYL—A REAGENT FOR COPPER[1]

By J. G. Breckenridge,[2] R. W. J. Lewis,[3] and L. A. Quick[3]

Abstract

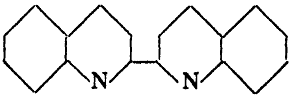
2 : 2′-Biquinolyl, prepared by catalytic dehydrogenation of quinoline, has been found to give a purple colour with the cuprous ion under certain conditions. The colour reaction is sensitive, specific for copper, and the intensity of the colour produced follows Beer's law. A procedure has been worked out for the detection and estimation of copper, the smallest amount of copper detectable being 1 part in 100,000,000. Stable complexes with cupric copper and cobalt have also been prepared.

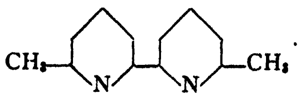
Introduction

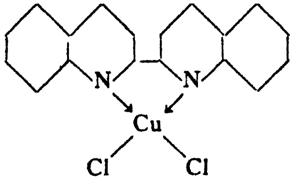
Co-ordination compounds of 2 : 2′-bipyridyl with many metals are well known, such as that with ferrous iron, which has become widely used as the basis for the colorimetric estimation of iron. 2 : 2′-biquinolyl (I), although of similar character, has been little investigated, an exception being the work of Smirnoff (4), who showed that it fails to give a colour reaction with ferrous iron. He considered the reason for this to lie in the difference between the ring structures of quinoline and pyridine, that of quinoline being supposed to be analogous to the structure for naphthalene proposed by Willstätter (7). In the light of more recent theories as to the structure of the naphthalene and quinoline rings (3), Smirnoff's hypothesis would seem to be faulty, and, in any case, to draw conclusions about the structure of the heterocyclic rings from one negative observation seemed to the writers to be unwarranted. Willink and Wibaut (6) found that 6 : 6′-dimethyl-2 : 2′-bipyridyl (II) also gave no reaction with ferrous iron, and it was felt that the behaviour of biquinolyl with metals other than iron should be investigated.

Results and Discussion

It has been found that biquinolyl gives stable compounds with cupric and cobaltous salts, and also forms a purple complex in solution with cuprous copper. The compounds formed with cupric and cobaltous chloride are of the type (Biq .MX_2), and it is probably that, in view of their insolubility in water and alcohol, they are represented by Formula III, the chlorine atoms



II


III


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Contribution from the Department of Chemical Engineering, University of Toronto. This paper is abstracted from theses submitted by R. W. J. Lewis and L. A. Quick in partial fulfilment of the requirements for the degree of B.A.Sc.

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[3] *Fourth year student, Department of Chemical Engineering, University of Toronto.*

being held within the complex by covalent links. The compound formed from ethylenediamine and cupric chloride has been shown by Chattaway and Drew (1) to exist as the dimeric form (Cu en_2)$CuCl_4$, and it is possible, though unlikely, that the $CuCl_2$-biquinolyl compound is of similar character.

The $CuCl_2$-biquinolyl compound is orange coloured and is precipitated when solutions of the base in hydrochloric acid, acetic acid, or alcohol are mixed with a solution of the cupric salt. Changing the proportions of the reagents did not affect the character of the product, even a large excess of the base and prolonged heating making no difference. The compound prepared from copper sulphate and the base is light green and crystalline.

The $CoCl_2$-biquinolyl compound is light green, and is best prepared by mixing alcohol solutions of the reactants. As with copper, no other form could be obtained. No reaction was observed between the base and cobaltic hexamminochloride in dilute alcohol, even on prolonged heating.

The complex formed with cuprous copper is deep purple in solution, and is obtained when solutions of a cuprous salt in dilute hydrochloric acid, acetic acid, alcohol, or dioxan are mixed with solutions of the base. The tendency to form the purple complex is very strong, as the colour is produced when metallic copper comes in contact with an alcohol solution of the base, and also when the cupric compounds described above stand in contact with alcohol for some time. The colour is not noticeably affected by exposure to sunlight over a long period, by boiling for several hours, or by bubbling air through the solution for several days.

These results indicated that biquinolyl might be of value as a reagent for the colorimetric estimation of copper, and tests were carried out to determine the optimum conditions for development of the colour. In the preliminary work a standard copper sulphate solution was made up, containing 5×10^{-5} gm. copper per ml., and to known volumes of this were added 4 drops of sodium sulphite solution (500 gm. in one litre of water) 2 ml. of ethanol, 14 drops of a solution of biquinolyl in ethanol (0 5 gm. in 100 ml.), and the volume was made up to 6 ml. with water. The resulting solutions were observed in a Klett colorimeter, and the values obtained showed that the colour intensity obeyed Beer's law, within the limits of error of the method employed.

The following ions were tested in dilute hydrochloric acid or ethanol solution, and were found to give no colour reaction with the base:— Na^+, K^+, Li^+, Be^{++}, Mg^{++}, Ca^{++}, Ba^{++}, Zn^{++}, Cd^{++}, Hg^+, Hg^{++}, Al^{+++}, Sn^{++}, Sn^{++++}, Pb^{++}, Sb^{+++}, Bi^{+++}, Fe^{++}, Fe^{+++}, Co^{++}, Ni^{++}, Mn^{++}, Ag^+, Ce^{++++}, Zr^{++++}, Cs^+, Cr^{++}, and Sr^{++}. Titanium trichloride gave a pale green colour with an ethanol solution of the base. The colour reaction was apparently therefore specific for cuprous copper, and further work was done to determine more precisely the relation between the colour intensity and the amount of copper present.

Experimental

The instruments used were a Pulfrich Gradation Photometer and an Evelyn photoelectric colorimeter (2). To determine the proper filter for use in these instruments, the colour absorption curve of a solution containing 4 × 10^{-5} gm. of copper in 50 ml. was plotted; the result is shown in Fig. 1. Since the percentage transmission was lowest at about 530 mμ, the filter selected for use with the Pulfrich Photometer was the L_2, which has a transmission maximum at this wave-length. In work with the photoelectric colorimeter, a filter having a maximum at 540 mμ was employed.

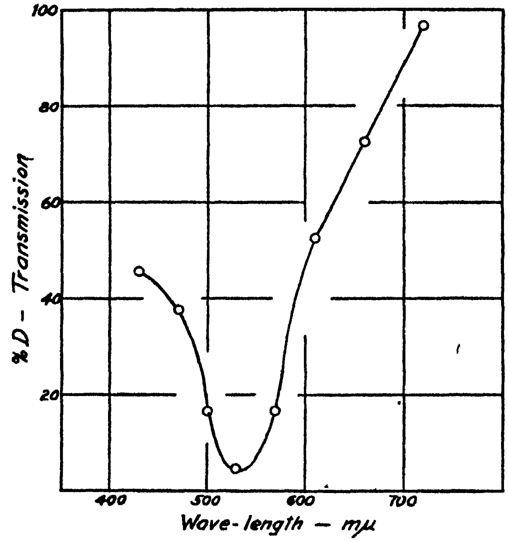


FIG. 1. *Colour absorption curve.*

The procedure finally adopted in making up the solutions for measurement was as follows—varying amounts of a standard copper solution (4 × 10^{-5} gm. copper per ml.) were taken, using standardized Exax Ostwald pipettes. To the copper sample was added 5 ml. of sodium bisulphite solution (10 gm. in 100 ml. water), 1 ml. of a solution of biquinolyl in glacial acetic acid (0.5 gm. per litre), and the solution made up to 50 ml. with glacial acetic acid. The pH of the resulting solution was found to be between 1.55 and 1.75. A series of results obtained using the photoelectric colorimeter, with samples containing from 0.2 × 10^{-4} to 2.4 × 10^{-4} gm. of copper are shown in Figs. 2 and 3, and it is evident that the colour intensity obeys Beer's law. Since the percentage transmission, G, could be read only to within 0.25% on the galvanometer scale, the limits of accuracy were ±1% of the amount of copper present. The lower limit for accurate readings was found to be with a solution containing 4 × 10^{-7} gm. of copper, while the lowest amount of copper necessary to give a perceptible deflection on the galvanometer was 8 × 10^{-9} gm., or approximately 1 part in 100,000,000. A solution containing 1 part of copper in 10,000,000 could easily be distinguished from a blank, using a 7 cm. depth of solution in a Klett colorimeter. The blank solutions for the photoelectric colorimeter, if exposed to sunlight for several days, showed a decrease in transmission of approximately 0.5%, and they were therefore made up freshly for each series of determinations.

When the general method indicated above had been worked out, tests were performed to investigate interference by other metals. It was found that the method was accurate with sodium, potassium, or magnesium present in 1000*x* the amount of copper; manganese or phosphate, 50*x*; and nickel, 10*x*. If more nickel was present it had to be removed with dimethyl-glyoxime, an excess of this reagent not interfering with the subsequent determination of copper.

Iron, although it gives no perceptible colour with biquinolyl, nevertheless interfered by reducing the percentage transmission, thus giving a high value for the copper. When the same amounts of iron and copper were present, the percentage transmission was about 1% lower than with copper alone. Any iron present in a sample was therefore precipitated in the usual manner

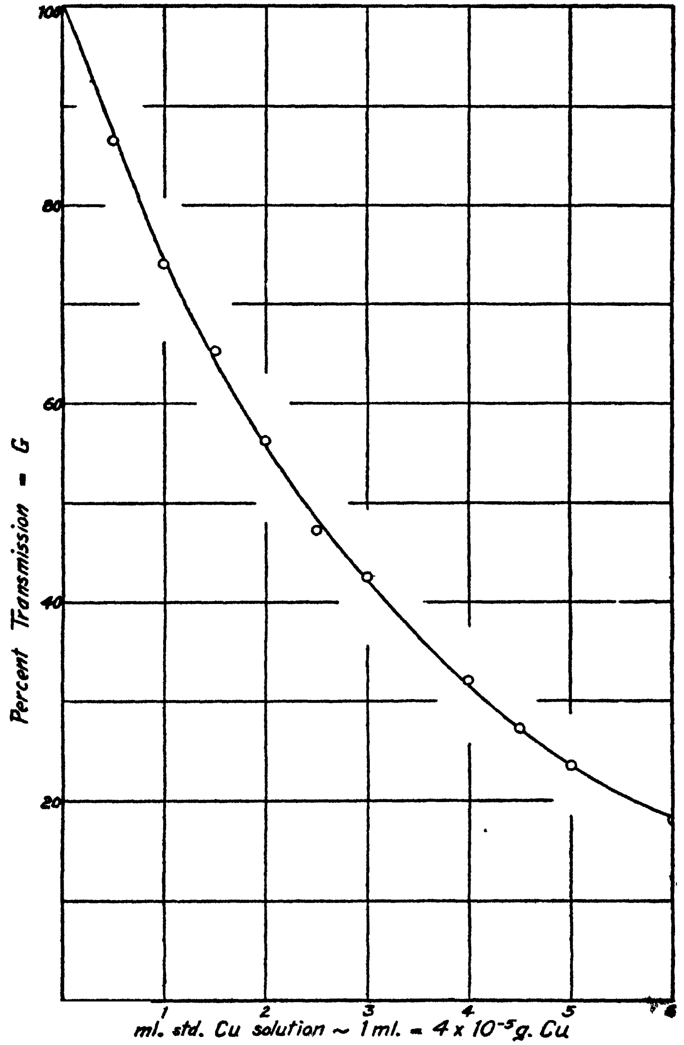


FIG. 2. *Calibration curve using photoelectric colorimeter.*

with bromine water and ammonia, the precipitate redissolved and reprecipitated, and the copper determined in the acidified filtrate in the normal manner.

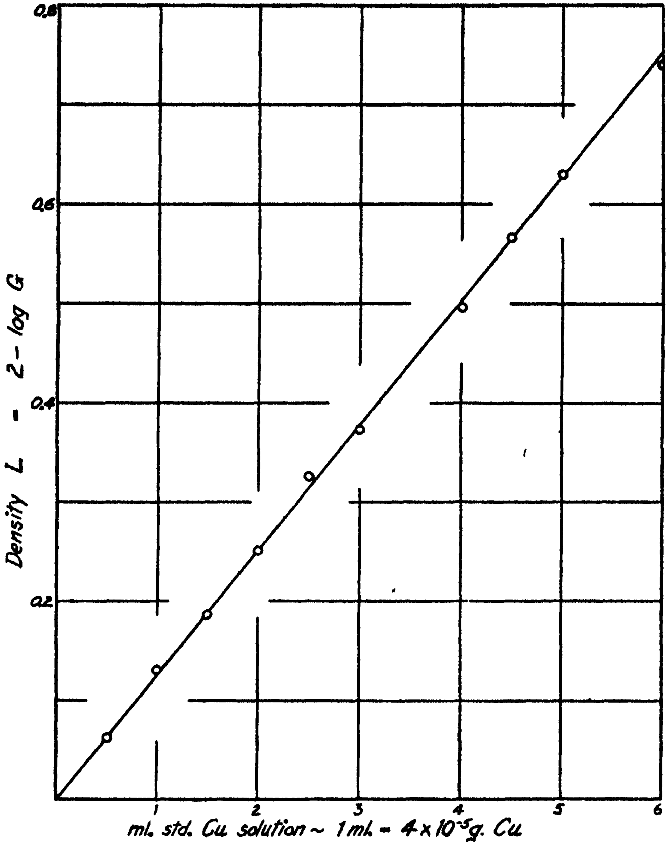


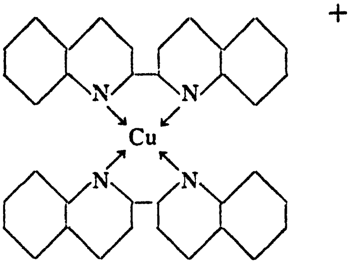
FIG. 3. *Application of Beer's law.*

It was thought desirable to check this method for copper against the ordinary electrolytic determination. A sample of nickel ore was obtained containing approximately 2% of nickel and 0.9% of copper, with some iron present. After the iron had been removed as described above (but not the nickel), samples were analyzed by the colorimetric method, and by an independent analyst using the standard electrolytic method, with the following results—

	Colorimetric	Electrolytic
	0.902%	0.892%
	0.906	0.890
	0.942	0.910
	0.905	0.930
Av.	0.91% copper	0.90% copper

It was found impossible to isolate in a pure state the complex responsible for the purple colour. Early experiments on the change of colour intensity with varying amounts of biquinolyl showed that there must be at least two molecules of the base present for every Cu atom, and analysis of an evidently impure product confirmed this ratio. The probable structure of the ion which is responsible for the colour is IV. The anion present in the solution does not affect the colour in any way, as far as could be found.

IV



The method described above for the determination of copper, and also for its detection when present in small amounts, would seem to be accurate and comparatively simple to use, but is handicapped by the unavailability of the reagent. As noted later, an increased yield is possible by use of the original catalytic method of Wibaut, Willink, and Nieuwenhuis (5), and it is intended to investigate this further.

The precipitate obtained with cupric salts in acid solution may also prove to be of use as a gravimetric precipitant for copper, and this point is also under investigation.

Preparation of Biquinolyl

This was prepared according to the method of catalytic dehydrogenation of quinoline given by Wibaut *et al.* (5), the nickel-alumina catalyst being prepared according to the method of Zelinsky and Kammarewsky (8). The yields obtained by the former were about 15%. It was found, however, that by following the procedure indicated below, the yield could be raised to nearly 50%. The apparatus shown in Fig. 4 was used, the catalyst being

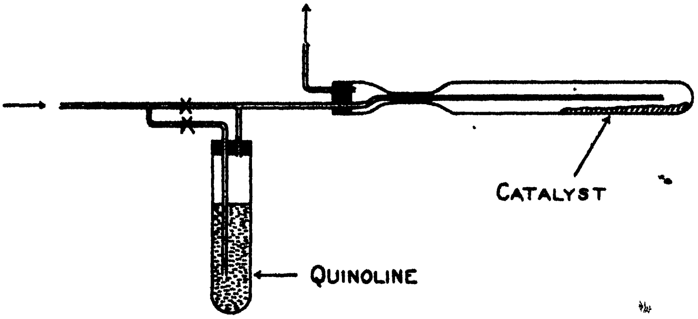


FIG. 4. *Apparatus used in preparation of biquinolyl.*

reduced in the Carius tube at 325° C. for 20 hr. The tube was then swept out with nitrogen, the flask containing the quinoline inverted, and the quinoline forced into the tube, which was then sealed, and heated as described by Wibaut *et al.* (5). A typical run gave the following results—9 gm. of catalyst (weight before reduction) with 45 gm. of quinoline heated to 330° C. for eight hours gave 9.9 gm. of biquinolyl (m.p. 195 to 196° C.*) and a recovery of 25 gm. quinoline, or a yield of 48%. Six runs of this size averaged a yield of 45%. The contents of the Carius tubes after cooling was almost solid with crystals of the product, very little or no tar being formed. (It should be mentioned that in some early work on this synthesis, a student developed a short-lived skin rash, apparently due to handling the tar.) The quinoline used was a synthetic product, and was dehydrated and twice distilled before use.

Compound with Cupric Chloride

This was prepared by mixing solutions of the base and cupric chloride in dilute hydrochloric acid, 50% acetic acid, or ethanol. The product from ethanol was microcrystalline, from the other solvents, amorphous, and possessed a bright orange-red colour. It was insoluble in hot acid solution, water, ethanol, and benzene, and was decomposed by alkaline solutions or by boiling with water. On standing in contact with ethanol the water solution gradually assumed the purple colour characteristic of the cuprous complex. It melted sharply at 338° C. with decomposition. Analysis gave the following results. Calcd. for $C_{18}H_{12}N_2 . CuCl_2$: C, 55.32; H, 3.10; N, 7.17; Cl, 18.14%. Found†: C, 55.42, 55.36; H, 3.14; 3.22; N, 7.13; Cl, 18.85, 18.65%.

Compound with Copper Sulphate

Methanol solutions of the reactants when mixed gave small green crystals of the product. This was not investigated further, except that it was observed that on the addition of hydrochloric acid the orange colour, characteristic of the cupric chloride compound, appeared.

Compound with Cobaltous Chloride

This could be obtained either from ethanol or dilute acetic acid solutions of the reactants, the product from ethanol crystallizing as shiny grass-green leaves. It was similar to the cupric chloride compound in its behaviour. It had a melting point higher than 360° C. Calcd. for $C_{18}H_{12}N_2 . CoCl_2$: C, 55.98; H, 3.13; N, 7.28; Cl, 18.36%. Found†: C, 56.00, 56.24; H, 3.13, 3.21; N, 7.35, 7.39; Cl, 18.42, 18.24%.

Compound with Cuprous Chloride

This was isolated by mixing the reactants in anhydrous ethanol in the proportion of 2 moles of base to 1 mole of cuprous chloride. The deep purple solution was evaporated, and the residue redissolved in ethanol, filtered, and again evaporated. This procedure was repeated six times, the final product being a brownish-green microcrystalline solid. It was much more soluble in ethanol than either reactant, and was insoluble in water or benzene. It decomposed gradually on heating above 195° C. Analysis gave the following results†: C, 73.75; 73.35; H, 4.25, 4.13; Cl, 5.04, 4.92%. Calcd. for $(C_{18}H_{12}N_2)_2 \cdot CuCl$: C, 70.8; H, 3.93; Cl, 5.8%. Calcd. for above formula with 20% of biquinolyl present as impurity: C, 73.5; H, 4.1, Cl, 4.7%.

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* *Melting points are corrected.*

† *Microanalyses by Miss J. Romeyn, Department of Chemistry.*

Acknowledgments

The authors would like to express their indebtedness to Mr. D. F. Smith of this Department for some of the earlier observations; to Prof. K. B. Jackson of the Department of Engineering Physics for valuable advice, and for the loan of the Pulfrich Photometer; to Dr. S. H. Jackson of the Hospital for Sick Children, Toronto, for the use of the Evelyn colorimeter; and to Mr. T. W. Cavers of the Falconbridge Nickel Mines for the sample and approximate analysis of the nickel ore.

† *Microanalyses by Miss J. Romeyn, Department of Chemistry.*

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THE TIME OF SET OF SILICA GELS

III. THE CHANGING EFFECT OF ALCOHOLS OVER A pH RANGE[1]

By L. A. Munro[2] and J. A. Pearce[3]

Abstract

The effect of alcohols on the setting time of silica gels has been studied through a pH range.

The total effect and the divergence of the individual behaviour of both monohydric and polyhydric alcohols become greater as the alkalinity of the gel is increased. When the time of set with addition agent is plotted as percentage of the original time of set, there is a constant effect for an equal number of alcohol molecules at pH 7. This apparently eliminates the dielectric constant of the alcohol as a decisive factor in coagulation. When the system is acidic, all the alcohols behave as retarders; when it is alkaline, only the higher polyhydrics act in this manner. The monohydrics and glycol change from accelerators to retarders at pH values between 7 4 to 8 5. The pH at reversal for each addition agent does not coincide with the pH at which the original gel shows minimum setting time.

Introduction

Hurd and Carver (7) have shown that the addition of ethyl alcohol increased the time of set of acid silica gels, whereas glycerol had a negligible effect. The pH of the gel was unaltered. Prasad and Hattiangadi (13) observed that the effect of methyl, ethyl, and propyl alcohols on alkaline gels was opposite to that on acid gels.

Munro and Alves (9) extended the series and found a regular decrease in the time of set of alkaline silica gels with increasing molecular weight of the monohydric alcohols. They observed that gels of high pH become more alkaline on setting, and that the effect seemed to be increased in the presence of the addition agents. It was also observed that though glycol decreased the time of set of these gels, its effect was not nearly so great as that of the monohydric alcohols. With glycerol the time of set was lengthened, i.e., the effect was similar to that brought about by addition agents in acid gels. The observations of Hurd and Carver on the effect of glycerol on acid gels were reinvestigated and their findings confirmed.

Munro and Pearce (12) found that the effect of glycerol was merely a part of a further and regular increase in the time of set when higher polyhydric alcohols were added to alkaline gels. It was also noted that, in the neighbourhood of pH 8.2, glycol changed from an accelerator of gelation to a retarder.

It was accordingly thought desirable to determine whether other alcohols show a reversal of their effect with changing pH; and further, whether this shift in behaviour has any relation to the pH at which the original gel shows minimum setting time.

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Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada. Presented to the Pure Chemistry Section, Canadian Chemical Convention, June, 1939.

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Previous results suggest that the pH at reversal will vary with the addition agent. If the pH at inflection varies, it would be of interest to ascertain whether the monohydric and polyhydric alcohols behave as groups.

Experimental

Baker's best grade of "crystalline sodium silicate $Na_2SiO_3.9H_2O$" was used (12). Analysis showed a molar ratio of $Na_2O : SiO_2 = 1.00 : 1.02$. The water used for making up solutions was redistilled and boiled before use. A stock sodium silicate solution of specific gravity 1.1569 (Westphal balance) and containing 6.7% SiO_2 by analysis was used. From this stock supply, solutions of various strengths were made as required.

After work had been started it was observed that the '3.35% SiO_2' silicate solution gave a gel setting too fast to permit an accurate study through the region of minimum time of set. A sodium silicate solution of specific gravity 1.0500 containing 2.51% SiO_2 by analysis was therefore prepared.

The silicate solutions were kept in stoppered, waxed, Pyrex flasks.

The acid was prepared, as before, by diluting glacial acetic with 500 cc. of water; this yielded a 1.636 *N* solution. The addition agents were Eastman's best grade supplemented by sorbitol from Schuchardt.

The procedure of mixing, temperature control, and determination of the time of set was the same as that followed previously (12). The rise in temperature on mixing was constant, except for pH values greater than 9.0. The temperature of the mixing thermostat was adjusted for the required change. It might be emphasized here that to prevent esterfication the alcohol and acid were kept separate until the moment of mixing.

The pH values were determined with the Coleman glass electrode.

Results

The results are given in Table I. The times of set given are the mean values of two to six determinations. The accuracy obtainable decreases with the dilution of the gel and with the increased time of set. The average deviation is ± 5%.

There was an increase of pH on setting which continued for some time afterwards. The increase is not great in the case of the acid gels: e.g., original pH, 6.0; pH on setting, 6.1; with a final value of 6.1 after 24 hr. With alkaline gels the increase is as much as 0.4 pH units, e.g., 9.4 to 9.6 to 9.8.

With the polyhydric alcohols the initial and final pH values of the gel were not essentially different from those of the original. The monohydric alcohols, however, with alkaline gels, gave an increase of 0.1 to 0.2 pH units, the effect being in the order: *n*-propyl, ethyl, methyl. The effect with neutral and acid gels was very slight.

Fig. 1 shows the curves for the effect of different addition agents on the set of the gels prepared with the '2.23% SiO_2' silicate solution, at pH 7.8. (The notation for all the curves is shown in Fig. 2.) It will be observed that

TABLE I

EFFECT OF ALCOHOLS ON THE TIME OF SET OF SILICA GELS DIFFERING IN CONCENTRATION AND pH

Molar conc. of alcohol	Silicate solution used								
	'2.5% SiO_2'						'2.23% SiO_2'	'3.35% SiO_2'	
	Initial pH								
	9.4	8.5	7.4	6.6	6.1	5.6	7.8	7.4	6.0
	Min.	Min.	Min.	Min.	Min.	Min.	Sec.	Sec.	Min.
0.00	14.0	8.5	11.3	41.0	119	310	540	210	60.0
Methanol									
0.50	11.3	7.6	11.7	43.5	125	324	545	224	63.0
0.99	9.2	7.2	11.8	45.0	129	336	552	230	65.5
1.49	7.3	6.8	11.9	46.5	133	351	552	245	69.0
Ethanol									
0.34	10.1	7.7	11.3	43.8	132	333	–	–	64.0
0.69	7.0	6.5	11.3	46.0	138	360	–	–	68.5
1.03	5.0	5.5	11.2	48.3	144	382	–	–	72.0
n- Propanol									
0.27	9.0	7.3	11.1	44.5	135	340	–	–	66.0
0.54	5.6	6.3	11.1	47.8	147	373	–	–	73.0
0.80	3.3	5.2	11.0	50.0	154	403	–	–	79.0
Glycol									
0.36	13.0	8.6	11.8	42.8	124	322	570	216	63.0
0.72	12.0	8.6	12.2	44.3	127	333	585	225	65.0
1.07	11.3	8.6	12.3	45.5	130	344	595	230	67.0
Glycerol									
0.27	15.4	8.9	11.7	42.0	122	315	570	216	61.0
0.55	16.0	9.3	12.0	42.5	124	319	585	220	62.0
0.82	16.5	9.5	12.2	43.5	126	326	600	225	63.0
Erythritol									
0.16	15.7	9.0	11.5	41.5	121	314	570	216	61.0
0.33	16.8	9.5	11.9	42.0	122	316	585	220	61.3
0.49	18.0	10.0	12.3	42.5	123	318	600	225	62.0
Mannitol									
0.11	17.5	9.3	11.8	41.5	119	313	510	216	60.5
0.22	18.9	9.8	12.0	41.8	120	314	600	220	60.8
0.33	20.0	10.5	12.3	42.0	121	315	615	225	61.0
Sorbitol									
0.11	16.6	–	11.8	–	–	–	–	–	–
0.22	18.2	–	12.0	–	–	–	–	–	–
0.33	19.5	–	12.5	–	120	–	–	–	60.3

not only is glycol a retarder, as indicated by the previous work, but, that at this pH, methyl alcohol has, in its effect, also changed from an accelerator to a retarder. Further, the retarding action of the others is practically unchanged [compare (12, Fig. 4)].

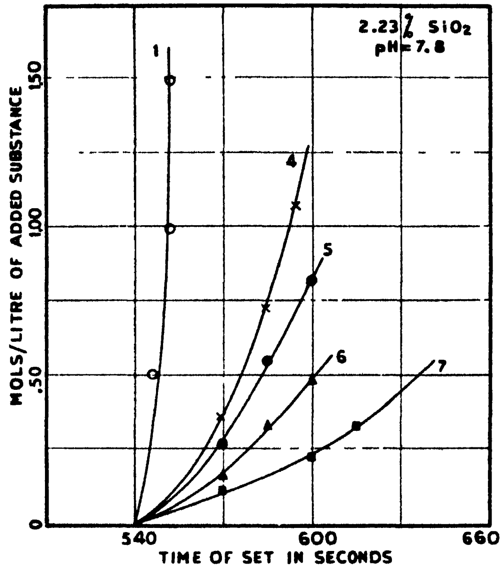

FIG. 1. *Silica gels, initial pH 7.8, prepared from 25 cc. of sodium silicate solution containing 2.23% SiO_2 + 25 cc. of acid mixture (12.7 cc. of acid + addition agent + water).*

With the gels from '3.35% SiO_2' silicate solution at pH 7.4 a similar shift in effect is noted (Fig. 2), both methyl alcohol and glycol now lengthening the time of set. With this gel concentration, the effect of methanol and glycol is reversed somewhere between pH of 7.4 and 8.8. The retarding action of the others is diminished, and the specific nature of the effect is less.

In order to eliminate any effect of gel concentration it was decided to make a series of measurements on gels of one standard silicate solution at a series of pH values.

The setting times for gels of each concentration of silicate and standard acid can be determined only over a limited pH range. This range is represented by the steep portion of the titration curves. Beyond this a large variation in the amount of standard acid causes a negligible change in pH, although a variation of even a fraction of a drop of the acid will change the time of set appreciably. The addition of stronger acid will extend the steep portion of the curve to lower pH values, but it results in gels having much longer times of set, with increase in the difficulty of determining accurate values (cf. Fig. 12).

A '2.5% SiO_2' silicate solution was chosen, as it gave convenient times of set. The titration curves for this solution and 1.636 N acid are shown in

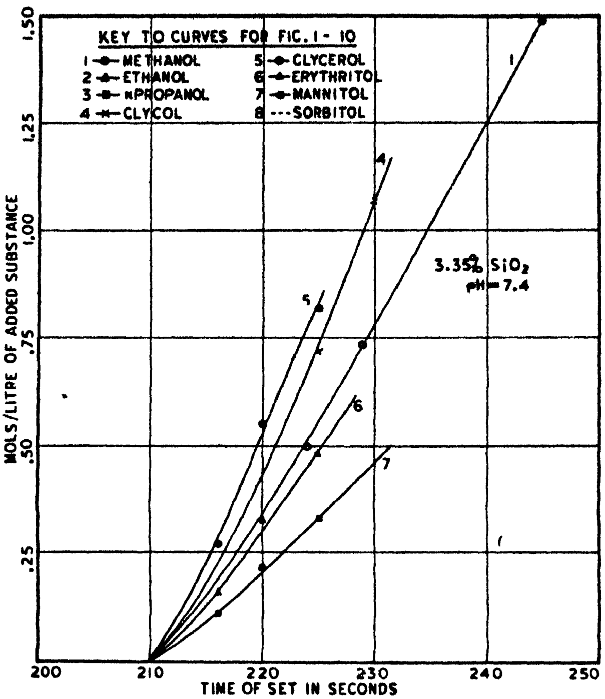

FIG. 2. *Silica gels, initial pH 7.4, 25 cc. of sodium silicate solution (3.35% SiO_2) + 25 cc. of acid-mixture (19.0 cc. of acid + addition agent + water).*

Fig. 3. Here the pH is plotted against standard acid added for a constant amount of silicate solution (25 cc.), the total volume being kept constant (50 cc.). Curve I is for a fresh silicate solution, and Curve 2 for a silicate solution six months old. The latter gives slightly longer times of set (12). The shift may be due to the absorption of carbon dioxide, in spite of the precautions taken, or to colloidal changes in the 'sodium silicate'.

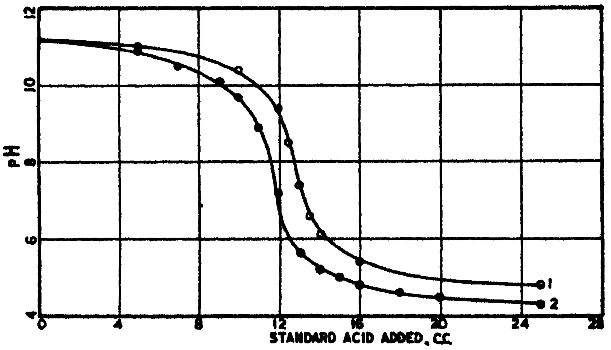

FIG. 3. *Titration curves for silicate solutions containing 2.5% SiO_2 versus the standard acetic acid. Curve 1, fresh, Curve 2, aged, silicate.*

The results with gels from the '2.5% SiO_2' silicate solution for this range of pH values are shown in Figs. 4 to 9.

It will be noted that the curves are widely divergent at pH 9.4 (Fig. 4), although the order of the effect in each case is the same as that noted in previous studies, viz., *n*-propyl, ethyl, methyl, glycol, glycerol (9), followed by erythritol and mannitol (12). The values obtained with sorbitol are not very different from those observed with its isomer, mannitol.

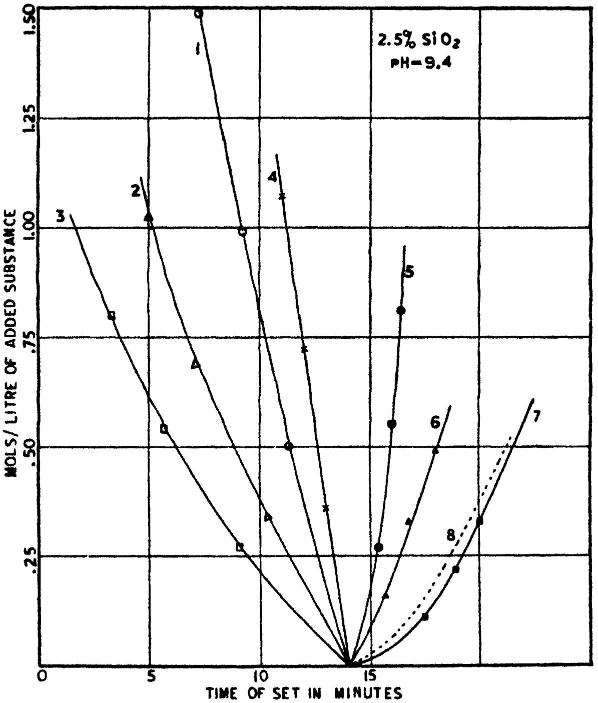

FIG. 4. *Silica gels, initial pH 9.4; 25 cc. of sodium silicate solution (2.5% SiO_2) + 25 cc. of acid mixture (13 cc. of acid + addition agent + water).*

The values for pH 8.5 are shown in Fig. 5. At this hydrogen ion concentration, glycol produces only a very slight change in the time of set. The order of the other curves is the same, but the effects are less pronounced, i.e., the curves have moved toward a zero effect. This diminution in specificity is more noticeable at pH 7.4, as will be seen in Fig. 6. Here, however, it is observed that methanol has become a retarder, and that now ethanol has a zero effect. Propanol still definitely shortens the time of set, although the acceleration is slight. The curves obtained with the different addition agents are still in almost the same order, but again close together. The sorbitol curve almost coincides with that for mannitol.

In Fig. 7, which shows the results at pH 6.6, the order of the curves is completely reversed, it being mannitol, erythritol, glycerol, glycol, methanol,

ethanol, propanol. Furthermore, all are now retarders. The reversed order still obtains at pH 6.1 (Fig. 8), but the individual effects become more divergent, and this divergence increases as the pH is decreased to 5 6 (Fig. 9).

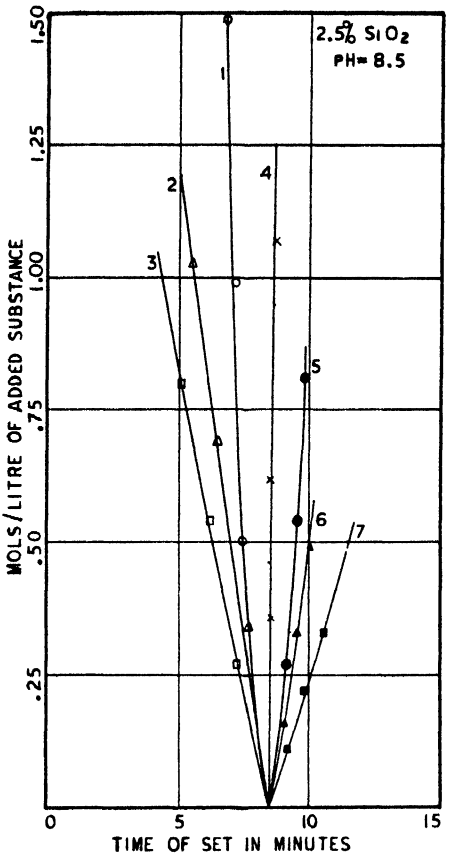

FIG 5 *Silica gels, initial pH 8 5, 25 cc of sodium silicate solution + 25 cc of acid mixture (12 5 cc of acid + addition agent + water)*

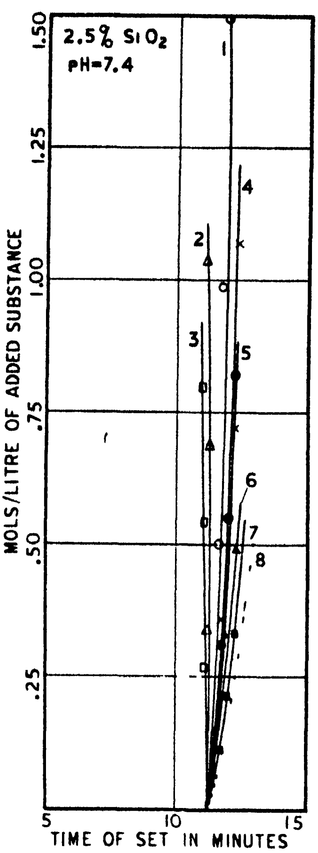

FIG 6 *Silica gels, initial pH 7 4, 25 cc of sodium silicate solution + 25 cc of acid mixture (13 0 cc. of acid + addition agent + water)*

It is known that increasing the concentration of silica decreases the time of set of normal acid and alkaline gels. It might be expected that the effects of concentration and addition agent would be additive. With an accelerator present, an increase in concentration of silica would further decrease the time of set, whereas with a retarder, an increase in concentration of the gel would decrease the effect. This point could not be decided from the writer's previous work because of difference in pH of the gels.

A comparison of Figs. 2 and 6 above would indicate that the effects are not additive.

In order to study the matter further, a series of experiments was performed using '3.35% SiO_2' silicate solution at approximately the same pH as that used in the experiments the results of which are shown in Fig. 8. The curves for this more concentrated gel are given in Fig. 10. Not only was the time of set of the original gel one-half that of the more dilute gel, but the final set with each addition agent was also almost exactly half that observed with the gel prepared from the '2.5% SiO_2' silicate solution. An examination of Figs. 2 and 6 will show that there again the ratio of the times for the different reagents is almost always equal to the ratio of the times for the original gels.

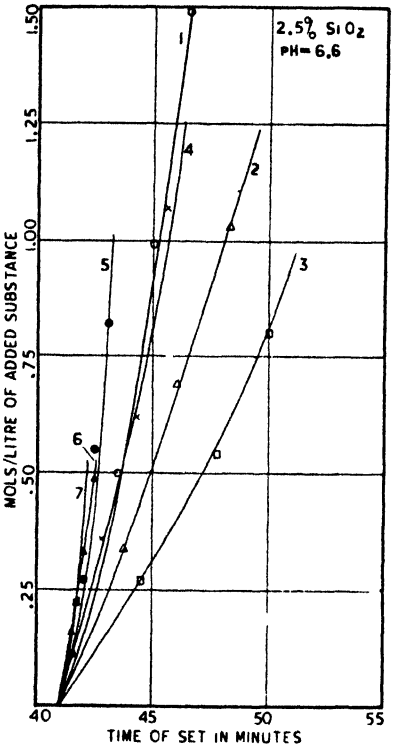

FIG. 7. *Silica gels, initial pH 6.6; 25 cc. of sodium silicate solution + 25 cc. of acid mixture (13.5 cc. of acid + addition agent + water).*

When the pH is plotted against the various times of set expressed as the percentage of the setting times of the original gels, regularities are observed that might not be noticed otherwise. In the range of concentration studied, the percentage effect with addition agent is independent of the concentration of silica, although it is apparent from the data that the actual time of set in minutes varies markedly with the gel concentration. In Fig. 11 the times of set for a constant amount of addition agent (0.5 *M*) are plotted in this manner. Smooth curves have been drawn from the authors' data, the

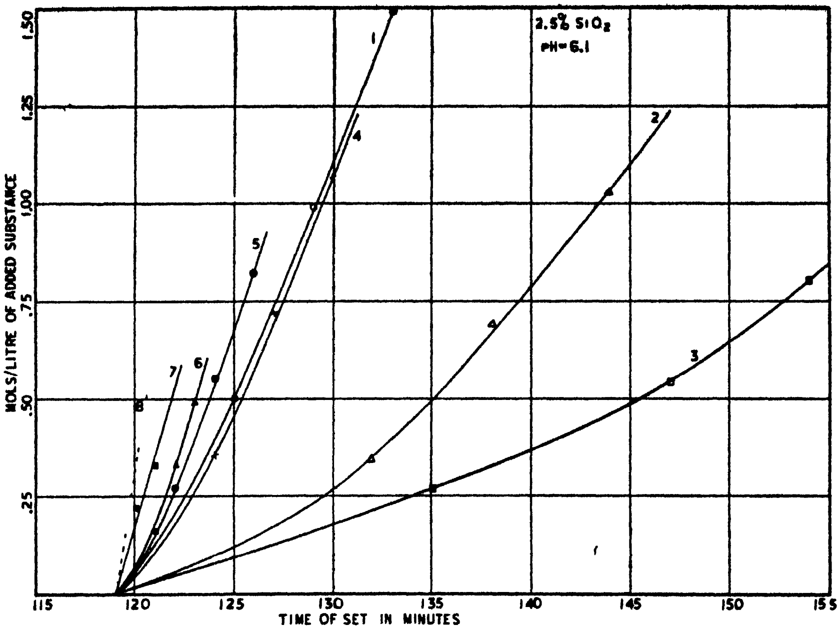

FIG. 8. *Silica gels, intial pH 6.1; 25 cc. of sodium silicate solution + 25 cc. of acid mixture (14 0 cc. of acid + addition agent + water).*

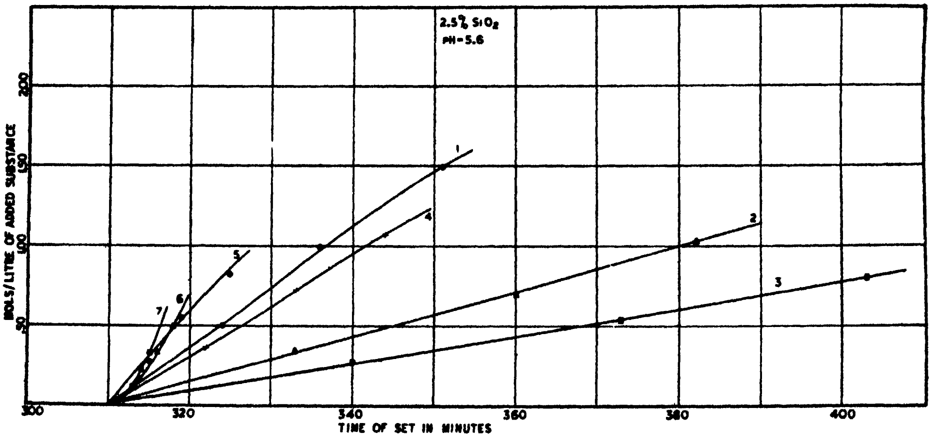

FIG. 9. *Silica gels, initial pH 5 6; 25 cc. of sodium silicate solution (2.5% SiO_2) + 25 cc. of acid mixture (15 cc. of acid + addition agent + water).*

deviations of the calculated points being of the same order as the experimental error. A continuation of the experimental curve for mannitol is given in the insert. The points shown on the figure are those calculated from the results of others as given in Table II. Evidently this treatment can be applied for the comparison of results obtained by different investigators, provided the definition of time of set is the same. The results of Prasad and Hattiangadi

(13), though of the same order, are not strictly comparable, since they used a standard of turbidity as the criterion of set.

TABLE II

TIMES OF SET OF GELS + 0·5 *M* ALCOHOL (*t*) AS PERCENT TIME OF SET OF STANDARD GEL (*T*) (NO ALCOHOL)

0·5 Moles	Silicate solution, '2 5% SiO_2'					
	pH = 9.4	pH = 8.5	pH = 7.4	pH = 6.6	pH = 6.1	pH = 5.6
	t as % *T*					
Methanol	81	89	104	106	105	105
Ethanol	63	85	100	109	113	111
n-Propanol	44	76	99	121	123	119
Glycol	90	100	106	106	105	104
Glycerol	114	112	106	104	105	103
Erythritol	129	119	109	104	103	103
Mannitol	154	133	112	103	102	102

	Silicate solution, '3.35% SiO_2'				Silicate solution, '2.23% SiO_2'		
	*pH = 10.4	*pH = 8 8	pH = 7.4	pH = 6.0	*pH = 10.6	*pH = 8.2	pH = 7.8
Methanol	53	83	105	106	50	95	101
Ethanol	–	–	–	111	–	–	–
n-Propanol	–	–	–	120	–	–	–
Glycol	78	85	105	105	76	103	107
Glycerol	116	109	104	103	120	105	108
Erythritol	141	122	107	103	165	108	111
Mannitol	245	151	110	102	284	120	117

Data by Munro and Alves (9)		Data by Munro and O'Brien (11)		Data by Hurd and Carver (7)	
pH = 10 4; silicate solution, '3 3% SiO_2'		pH = 5.6; silicate solution, '4.4% SiO_2'		pH = 5.5	
Methanol Ethanol *n*-Propanol Glycol Glycerol	49 24 18 77 122	Methanol Ethanol *n*-Propanol Glycol Glycerol	107 111 122 105 104	Ethanol Glycerol	112 103
pH = 5.1; silicate solution, '3.3% SiO_2'		—	–	—	–
Glycerol	104	—	–	—	–

*Data from (12).

Discussion

Several additional points of interest emerge from a consideration of Fig. 11. The most striking is the convergence of all curves at pH 7. It will also be noted that the point at which the curves coincide is not the 100% line.

In every case the time of set has been lengthened by an amount of approximately 6% by the same number of molecules of addition agent, irrespective of the alcohol used.

Further, the specific effect of the addition agent is greater on the alkaline side. At a pH of two units from the neutral point (pH = 9), the times of set of the alkaline gels vary from 60 to 150% of that of the original gel. On the acid side (pH = 5) the variation lies between 101 and 121%. The effect of the addition agents in the latter case is very slight. In so far as they have been studied, all behave as retarders of gelation.

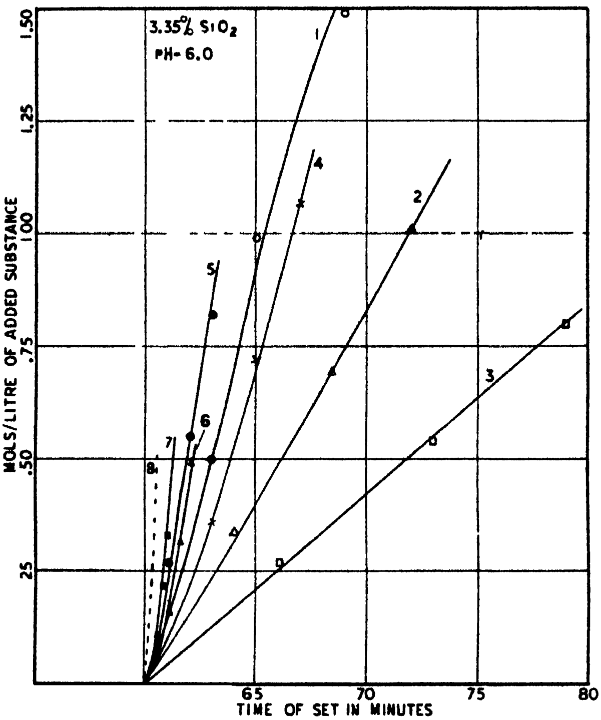

FIG. 10. *Silica gels, initial pH 6 0, 25 cc of sodium silicate solution (3 35% SiO_2) + 25 cc. of acid mixture (22 0 cc. of acid + addition agent + water).*

The intercepts on the 100% line made by Curves 1 to 4 give the pH at which these alcohols change from accelerators to retarders.

If similar curves were plotted for greater concentrations of addition agent, the curves on the alkaline side would be spread out but would converge at pH 7 at a higher value of the percentage time of set, but Curves 1 to 4 would cut the 100% line at the same pH values. On the acid side, the curves would be displaced to the right. For zero concentration the curve becomes the 100% line.

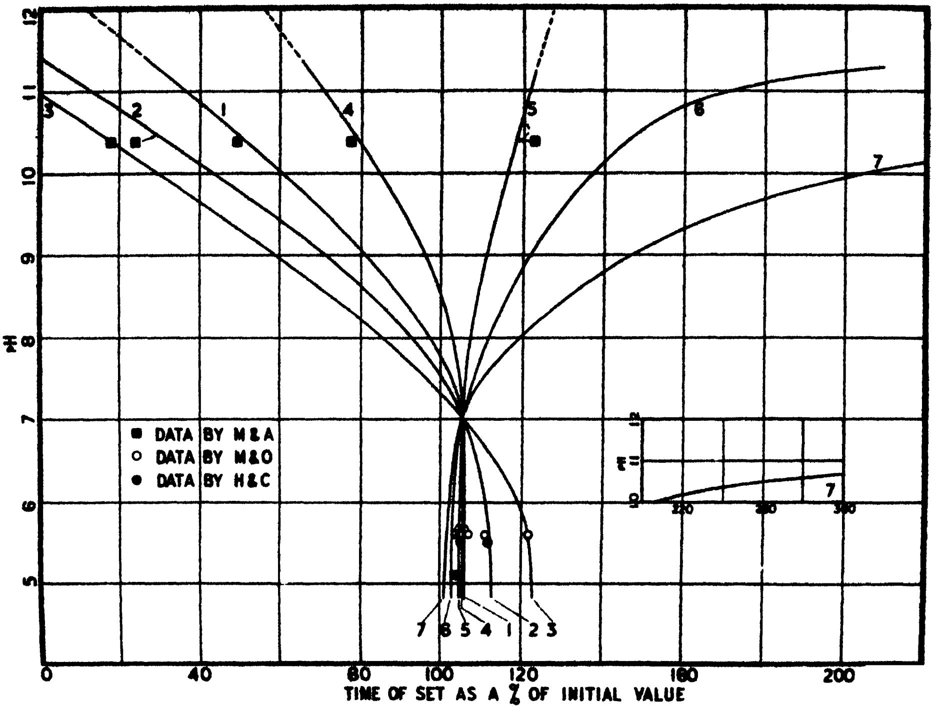

FIG. 11. *Time of set for gels containing 0.5 moles of different alcohols vs. pH of original gel. Solid curves; authors' data. Points represent data by Munro and Alves, Munro and O'Brien, Hurd and Carver.*

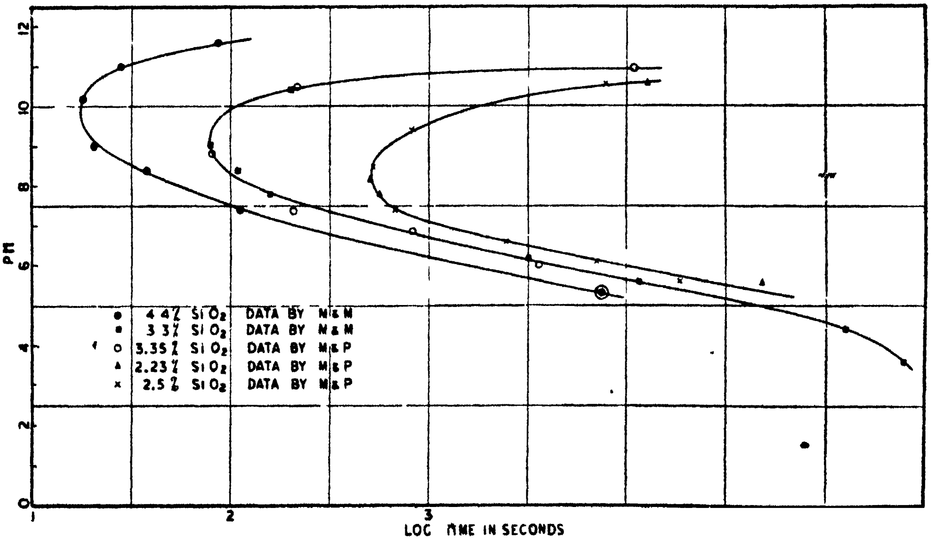

FIG. 12. *Curves showing pH of gels of minimum times of set for different concentrations of silica. Data by Munro and McNab and present authors.* ⊙ *data by Munro and O'Brien.*

From the convergence of the curves at pH 7 it is apparent that the dielectric constant of the addition agent plays a negligible part.

In this study the time of set as measured represents the time required for the gel to develop a definite resistance to shear. Fig. 12 shows that when the times for the original gel to reach this constant rigidity are plotted over a range of pH values, the curve passes through a sharp minimum and is symmetrical about this minimum point. The pH at minimum time of set of these original gels increases slightly as the concentration increases.

The points shown on the curve represent data obtained by the authors and others (10, 11). A similar shift was observed by Batchelor (3).

Hurd (6) states that a straight line relation between pH and logarithm of the time of set was obtained with both acid and alkaline gels. Fig. 12 shows that the curve is linear over a portion of the pH range in both acid and alkaline regions.

The points of inflection of the titration curves also show changes comparable to the shift of the pH values at minimum time of set. Further, the point of inflection and the point of minimum time of set are at almost the same pH for the same silicate concentrations.

In view of the shift in gelation curves for original gels as the concentration of silicate is changed, it seems all the more remarkable that the percentage effect of addition agent alone, is virtually independent of the concentration.

Batchelor (3) has summarized various estimates of the isoelectric point of silica sols. These range from pH 4.6 to 6.2. This is not the range showing minimum time of set of the writers' original gels, nor is it the range within which the percentage effect of addition agent is a maximum. The pH at which an addition agent changes from an accelerator of gelation to a peptizing agent or retarder does not coincide with either the point of minimum time of set of the original gel or with the isoelectric point.

Esterification cannot be offered as an explanation of the specific effect of these alcohols A cursory examination of the data shows a decrease in hydrogen ion concentration of the gelatinizing mixture containing an alcohol. However, a similar change is obtained with other addition agents, e.g., acetaldehyde and acetone (9). Further, the change in pH measured at the time of set and after 24 hr. is the same for the original gel and the gel with addition agents in most cases.

A consideration of the rate constants showed that there would be hardly any esterification during the time of the sol-gel transformation. The reaction might, however, be catalyzed by the presence of SiO_2. A search of the Chemical Abstracts revealed only one reference to silica as a catalyst for esterification. Korolev (8) catalyzed the esterification of β-naphthol and salicylic acid with SiO_2. However, even if equilibrium were reached in this short time the change in pH due to removal of the acetic acid by esterification would be comparable to the change in pH observed immediately on mixing the '3.35% SiO_2' silicate and acid mixture.

Further, the observed pH changes on mixing and after setting of the alkaline gels are much greater than could be obtained by change in acid content due to esterification. Should esterification occur in the acid gels, the resulting loss of acid should cause, in the time of set of gels containing alcohol, a decrease, rather than the observed increase. The evidence therefore seems to indicate that esterfication cannot serve as an explanation of the specific behaviour of the alcohols.

It is well known (14, 15) that monohydric alcohols (and other organic substances) are strongly adsorbed by silica gel. There is evidence (4, p. 563 *et seq.;* 15, pp. 193–198) that colloidal silica and, in fact, even commercial alkali silicates, contain silica particles stabilized by negative hydroxide ions. The adsorption of monohydric alcohols or other addition agent may cause a displacement of a certain number of hydroxide ions and result in a corresponding change in pH.

In a gel, as little as 0.5% of solid matter may immobilize or give a certain amount of rigidity to the 99.5% of dispersion medium. Gelation must, therefore, be associated with hydration of the particles. It has been shown by Kruyt (5, p. 78) and others that monohydric alcohols and various other organic materials cause a displacement and removal of the bound water. This would cause an acceleration of the rate of gelation. Adsorption is known to vary with hydrogen ion concentration, and the magnitude of the effect on the time of set would vary with the pH. However, this change in pH does not explain the reversal of the effect of monohydric alcohols and glycol at a definite pH.

Further, although there is little information regarding the dehydrating power of higher alcohols, it is known that glycerol is very hygroscopic. One would expect, therefore, that glycerol would have a marked accelerating effect. It is obvious then that here some other factor plays a greater role than dehydration. It is known that sugars and glycerol (1, p. 922) act as stabilizing and peptizing agents of inorganic particles in colloidal systems and that ethanol behaves similarly in acid media (2, p. 277 *et seq.*). It may be that with the higher polyhydrics in silica sols the protective action which prevents the formation of the gel network is the determining phenomenon. This may be true also of monohydric alcohols and glycol in the presence of excess hydrogen ion.

It is obvious that acid gels differ from alkaline gels. Any theory of gelation must account for this fact.

It is felt that many explanations of the process of setting and the structure of the gel after it has set have been based on incomplete data, and that sufficient experimental data have not yet been obtained to permit a satisfactory explanation of these phenomena.

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FRACTIONATION OF THE CHLOROFORM EXTRACT OF MAPLE SYRUP[1]

By Louis Sair[2] and J. F. Snell[3]

Abstract

A method of fractionating the chloroform soluble constituents of maple syrup has been devised. Marked differences were observed among Quebec syrups of different years. Fat constituted half the weight of the extract of the 1935 syrup but was completely absent in the 1936, and present in very small quantity in the 1937, product. Crystals of carbonyl compounds having vanillin odour were isolated from bisulphite fractions of the 1935 and 1936 extracts, but the crystals from the two years' syrups differed from each other in melting point and chemical behaviour. Vanillin was not found. An odourless fraction constituting 35% in 1935 and 65% in 1936 had a composition and a behaviour similar to those of lignin. The substance chiefly responsible for maple odour is indicated to be an enolic viscous oil, volatile at 0.03 mm., and present in the 1936 and 1937 syrups in the proportions of 0.6 gm. per 100 gal. of syrup, or about 1 p.p.m.

Introduction

The characteristic flavouring principle of maple sap syrup has not been definitely isolated. Robison (19) found that the flavour could be extracted from the syrup or from maple sugar by ether, chloroform, or benzene. With saturated sodium bisulphite solution, Nelson (17) and Skazin (22) separated vanillin-like products from ether and chloroform extracts, respectively, but the former concluded that maple flavour was due rather to a phenolic than to this carbonylic material. Skazin (22) demonstrated that the flavour is developed in the boiling process. Findlay (8) and Risi and Labrie (20) confirmed this conclusion. The former attempted to discover in the raw sap the substance from which the flavour is produced and asserted a relation of this precursor to ferulaldehyde and to lignin. Labrie (14) and Risi and Labrie (20) attributed the flavour to Czapek's "hadromal" (4, 5, 10), a material whose standing as a chemical compound is not established (9, 18). They preceded Findlay in suggesting a relation to lignin and claimed to have synthesized the flavouring principle from guaiacol, vanillin, and furfural (nascent from sucrose).

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[2] *Formerly Research Assistant. This paper is based on a thesis accepted in partial fulfilment of the requirements of McGill University for the degree of Ph.D. The work on the 1937 syrup was done in the Laboratories of the National Research Council, Ottawa, after attainment of the degree.*

[3] *Emeritus Professor of Chemistry.*

None of these investigators developed a satisfactory method of fractionating the ether or chloroform extract. The writers have endeavoured to devise a method which would accomplish fractionation without destroying the maple flavour and have made a partial study of some of the products so obtained. These include a fat, two crystalline carbonyl products, bearing some resemblance to those found by Nelson and Skazin, five amorphous lignin-like products and a neutral oil, volatile at 0.02 mm., which develops maple odour on standing, and which the results indicate to be the essential flavouring principle.

Experimental

Material

The Quebec Department of Agriculture, then presided over by the Hon. Dr. J. Adelard Godbout, generously donated maple syrup of good flavour and medium colour collected by "Les Producteurs de Sucre d'Érable de Québec" in the seasons of 1935 and 1936. It was delivered in one-gallon containers as received from individual farmers. As will appear, the extracts made from the syrups of the two seasons showed surprising differences in composition.

Extraction

Two-gallon portions of syrup were diluted with three-fourths their volume of water and shaken with chloroform in a glass bottle enclosed in a barrel churn. Each portion was shaken for five hours with 1500 cc. of chloroform and for a like period with another 1500 cc. The combined extract was concentrated at atmospheric pressure to a volume of approximately 200 cc. and was kept in a refrigerator. It was later converted by vacuum distillation to a reddish, viscous residue having a decided maple odour.

Fractionation

The viscous residue was taken up in 95% alcohol. From the alcohol solution pertaining to each lot of 1935 syrup, whatever its place of origin, a soft solid (Fraction *A*) separated on cooling. This was a fat (see below). It constituted about half the chloroform extract. No corresponding product was found in any of the 1936 syrups.

After removal of *A*, the alcohol was evaporated *in vacuo* and the residue was dissolved in chloroform, and shaken in an ice bath with two successive 50 cc. portions of saturated sodium bisulphite solution. The material thus extracted constitutes Fraction *B* (see flowsheet).

The exhausted, red, chloroform solution was dried with sodium sulphate and evaporated *in vacuo.* The residue, a viscous oil, when subjected to the higher vacuum of a Hyvac pump, swelled, filling the flask, and leaving an amorphous residue, which was ground to a scarlet powder of distinct maple odour. Qualitative tests indicated the presence of phenols, acids, carbonyl compounds, and neutral products.

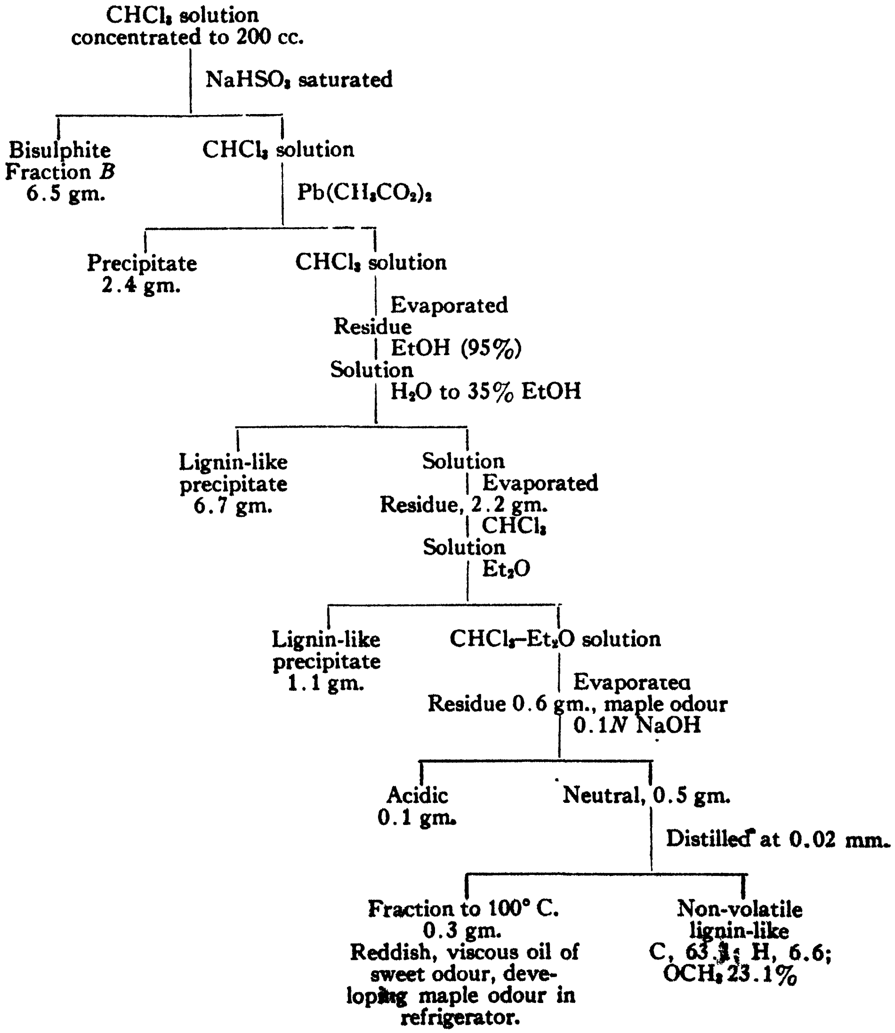
The procedure finally adopted for further fractionation is shown in the flowsheet. This procedure was adopted in the light of preliminary attempts to separate the constituents by use of organic solvents, mild alkalies, and water. These preliminary experiments yielded the following information:

1. Petroleum ether dissolved only 5% of the residue. Ethyl ether (peroxide-free), applied to the remainder, dissolved 45% of the original. The remaining 50% was still soluble in chloroform. Only the ethyl ether extract had maple odour.

FLOWSHEET

CHLOROFORM EXTRACT OF MAPLE SYRUP (50 GAL., 1936)

Final method of fractionation


$CHCl_3$ solution concentrated to 200 cc.
$NaHSO_3$ saturated
Bisulphite Fraction *B* 6.5 gm.
$CHCl_3$ solution
$Pb(CH_3CO_2)_2$
Precipitate 2.4 gm.
$CHCl_3$ solution
Evaporated
Residue
EtOH (95%)
Solution
H_2O to 35% EtOH
Lignin-like precipitate 6.7 gm.
Solution
Evaporated
Residue, 2.2 gm.
$CHCl_3$
Solution
Et_2O
Lignin-like precipitate 1.1 gm.
$CHCl_3$–Et_2O solution
Evaporated
Residue 0.6 gm., maple odour
0.1*N* NaOH
Acidic 0.1 gm.
Neutral, 0.5 gm.
Distilled at 0.02 mm.
Fraction to 100° C. 0.3 gm. Reddish, viscous oil of sweet odour, developing maple odour in refrigerator.
Non-volatile lignin-like C, 63.1; H, 6.6; OCH_3 23.1%

2. Sodium bicarbonate (5%), ammonium hydroxide (1 : 10), and sodium hydroxide (2%) applied in succession to the chloroform solution of the ether extract, removed, respectively, 7, 10 and 57% of the total, leaving a neutral fraction of 25%, a red mixture of oil and solid having a pleasant odour. The alkaline extracts were odourless.

The results with ammonium hydroxide are in contrast to Nelson's experience with direct ether extracts of maple syrups (17). In many tests on 1935 and 1936 syrups, ammonium hydroxide was found to extract only a minor portion of the ether extract and to destroy the odour.

3. The ether-insoluble portion of the extract and the alkaline extracts of the ether solution are similar products—acidic, lignin-like and odourless (see below, Product *C*).

4. Water dissolves the maple odour material and yields it up again to chloroform. The aqueous extract can be separated into (i) neutral, (ii) phenolic, and (iii) carboxylic fractions by (i) titrating to pH 8 1 with 0.1 *N* sodium hydroxide, (ii) saturating with carbon dioxide, and (iii) acidifying, shaking out with chloroform after each operation. The neutral fraction constitutes about five-sixths of the whole and carries the odour, though modified. The phenolic fraction is odourless, the carboxylic slightly rancid. The neutral fraction reduces Fehling's solution and answers to tests for the carbonyl group but not to the Millon and Liebermann tests for phenols. The portion distilling below 140° at 0 02 mm. (30% of the total) develops true maple flavour in the refrigerator.

5. Lead acetate, which Findlay (8) found would precipitate a portion of the original chloroform solution, precipitates the higher distilling portions of the neutral fraction but not that coming over below 140° C.

Products

A. The Alcohol-insoluble Fraction

This fraction constituted half the total weight of the chloroform extract of the 1935 syrup but was entirely absent from that of the 1936 season. It is a yellow saponifiable oil, probably identical with that which Nelson (17) found in Vermont, but not in Michigan, syrup, and which he attributed to fat added to the sap to prevent foaming. In the writers' work, trials on lots of one, two, four, or more gallons from individual producers invariably gave this product, which must therefore be regarded as a normal constituent of the sap of the 1935 season in Quebec. It had a refractive index of 1.457 at 20° C., Hübl iodine number, 41 to 43; saponification number, 270; acid number, zero; unsaponifiable matter, 1.9% (a yellow oil with a penetrating, shellac-like odour, giving negative Liebermann and Whitby tests for sterols). The properties of the liberated fatty acids from 15 gm., separated by the lead-salt-ether method, were as shown in Table I.

TABLE I

PROPERTIES OF LIBERATED FATTY ACIDS

	Weight	Hübl value	Mol. wt. by titration
Saturated	6.4	6–7	261
Unsaturated	5.6	88–90	275

Fractionation of the saturated acids according to Rosenthaler (21) yielded (i) 1.05 gm. of m.p. 62 to 64° C.* and mol. wt. 261, (ii) 1.40 gm. of m.p. 60 to 61° C., mol. wt. 256; (iii) 1.20 gm. of m.p. 57 to 61°, mol. wt. 254; and a fourth fraction (soluble in 50 cc. absolute alcohol at 0°), which was lost. Recrystallization of Fraction (i) yielded no higher melting product. The results point to palmitic acid (m.p. 62.6, mol. wt. 256) as the predominating acid. Myristic acid may be present in very small proportion. The unsaturated acids must be mainly oleic (iodine number, 90; mol. wt., 282). Treatment with bromine in acetic acid yielded no crystalline product. Glycerol was detected by the acrolein test and by three colour tests described by Morrow (16, p. 238).

B. The Bisulphite Fraction

Nelson (17) and Skazin (22), using bisulphite extraction, and Labrie (14), extracting an ether extract with petroleum ether, obtained evidence of the presence of substances resembling vanillin. None of them succeeded in satisfactorily identifying this aldehydic material. Not only did their opinions as to its nature differ, but Nelson obtained different results on the two syrups he examined. The writers' experience is similar. The bisulphite fractions from the syrups of 1935 and 1936 differ so radically as to require separate description.

1935

The use of acids to decompose the bisulphite addition compound was avoided, sodium carbonate being used instead. To the bisulphite solution and 200 cc. of chloroform in a separatory funnel a 10% solution of sodium carbonate was added slowly in 10 cc. portions without shaking. The process was repeated several times with fresh portions of chloroform, the object being to limit the time of exposure of the odorous substance to the action of the alkali. The different extracts were combined, dried with sodium sulphate, concentrated to 200 cc. and taken to dryness *in vacuo*. From 30 gal. of syrup, 0.65 gm. of a yellow, viscous oil, with an odour like that of vanillin, was obtained. The mass was extracted with boiling petroleum ether. Evaporation of the ether yielded a few crystals, contaminated with a yellow oil. Attempts to free the crystals from this oil by use of activated carbon, or of solvents, simple or mixed, failed. The crystals were very unstable and, when left standing in the air or exposed to heat, quickly changed to a reddish oil. Similar results had previously been obtained in this laboratory by Skazin (22), who followed Nelson's procedure of decomposing the bisulphite compound with dilute sulphuric acid. The crystalline product was finally isolated by extracting the chloroform solution of the bisulphite fraction with ammonium hydroxide (1 : 10), acidifying, extracting with chloroform, and evaporating *in vacuo*. Silvery white crystals of m.p. 90 to 92° C. were obtained (14 mg. from 10 gal. of syrup). This product reduced Fehling's solution, decolorized bromine water, and gave a brown colour with ferric chloride. A 2,4-dinitrophenylhydrazone, prepaied according to the method of Allen (1), showed m.p. 215 to 217° C. and OCH_3, 12.7%. This product is obviously not vanillin. None of it was found in the 1936 syrup.

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* *Melting points are uncorrected.*

1936

Treatment of the chloroform extract of this syrup with sodium bisulphite yielded a red, gummy precipitate (3.5 gm. from 30 gal. of syrup). This is in contrast to the behaviour of the 1935 syrup, which yielded no insoluble addition product.

The bisulphite soluble fraction (and the washings from the precipitate), decomposed by sodium carbonate, yielded a viscous, yellow, vanillin-smelling oil (0.5 gm. from 30 gal. of syrup). As previously stated, it was not found possible to isolate a crystalline product from this oil by the method of extraction by ammonia used in 1935. The oily material was phenolic in behaviour, in that it was soluble in ammonium hydroxide solution and completely precipitated by carbon dioxide. The use of organic solvents also proved ineffective. However, distillation at 0.03 mm. pressure from a 160° C. oil bath yielded 40% of volatile material, which, when resublimed at a bath temperature of 80 to 90°, consisted of a white crystalline material mixed with oil. By dissolving in 0.5 cc. of chloroform, adding petroleum ether until turbid, cooling in the refrigerator, and repeating this procedure 10 to 15 times, almost colourless (very faintly yellow) crystals, melting at 110 to 112° C. and having a vanillin odour, were obtained in the proportion of 45 mg. per 50 gal. of syrup. Analysis showed—C, 57.3; H, 5.5; $OCH_3 + OC_2H_5$, 30.3%. Calcd. for $C_9H_6O_4(OCH_3)(OC_2H_5)$: C, 56.7; H, 5.5; $OCH_3 + OC_2H_5$, 29.8%. A 2, 4-dinitrophenylhydrazone was obtained as fine, long, scarlet needles, m.p. 232 to 233° C.; OCH_3, 12.4%. Calcd. for two carbonyl groups, 12.3%.

The crystalline product gave a positive xanthate test for hydroxyl, positive iodoform and nitroprusside tests for methyl ketone structure, and negative Fehling, Schiff, Liebermann, and Millon tests. A crystalline acetate could not be obtained. The behaviour indicates a benzene derivative with one alcoholic and one phenolic hydroxyl, two carbonyl groups (one of which is methyl ketonic), a methoxyl, and an ethoxyl group. This would account for the six oxygen atoms.

The study of the bisulphite fraction clearly indicates the absence of vanillin from the 1935 and 1936 Quebec syrups, and confirms the conclusion of previous investigators that the substances of vanillin-like odour and carbonylic constitution are not the *chief* contributors to the flavour of maple products.

C. The Lignin-like Fraction

This fraction constituted 60 to 70% of the total chloroform extract of the 1936, and 35 to 40% of that of the 1935, syrup. It was red, amorphous, and odourless. The writers' observations yielded no indication of a relation to the flavour of the syrup. With the successive use of barium hydroxide, hydrochloric acid, sodium hydroxide, and carbon dioxide it was separated into five portions. Four of these had elementary compositions (C, 59.0–62.6; H, 6.4–6.7; OCH_3, 19.6–21.4%) within the range of recorded analyses of lignin (3, 11, 13). The chemical behaviour also corresponded to that of lignin. The fifth portion, constituting about one-eighth of the whole, had the composition—C, 46.9; H, 6.1, OCH_3, 19.2%. It was more highly coloured than the others and resistant to acid hydrolysis.

The presence of "free", soluble lignin in wood has been reported by von Euler (6), Klason (12), and Wislicenus (23). The last-mentioned found appreciable quantities in the sap of the sugar maple.

D. The Maple Odour Fraction

The product which, in the writers' opinion, is chiefly responsible for maple odour is the neutral volatile viscous oil (see flowsheet). The true maple odour was modified to a sweet one either by the unavoidable treatment with 0.1 *N* alkali or by the distillation, but it was restored on standing a few days in a refrigerator.

This component was isolated from both the 1936 and the 1937 syrup. Results of analyses were as shown in Table II.

TABLE II

ANALYSES

	C	H	O (by diff.)	OCH_3
Product of 1936	70.2	9.3	30.5	10.2
Calcd. for $C_{18}H_{28}O_4$	70.1	9.1	20.8	10.1
Product of 1937	66.14	7.87	25.99	8.93
Calcd. for $C_{20}H_{28}O_6$	65.93	7.69	26.38	8.52

The 1937 analysis refers to a product that was redistilled and was therefore considered purer than that of 1936.

The following properties of the 1936 product were observed: it has refractive index of 1.555 at 20° C.; is optically inactive; reduces Fehling's solution; decolorizes bromine water; gives negative tests (xanthate, acetic anhydride) for alcoholic, and negative tests (Millon, Liebermann) for phenolic, hydroxyl; gives negative tests (iodoform, nitro-prusside) for methyl ketone, and for ester, structure [Feigl, (7)]; it gives positive tests for carbonyl group [precipitate with 2,4-dinitro-phenylhydrazine, and [Kurt-Meyer (15, pp. 325-326)] for enolic hydrogen (15.0% by iodimetry)].

Attempts to prepare crystalline products by oxidation with 1 : 4 nitric acid or with neutral permanganate and by reduction with powdered zinc failed, as did also attempts to produce oximes, semicarbazones, and acetyl derivates. The 2,4-dinitrophenylhydrazone obtained was amorphous and of low yield and indefinite melting point.

As the combustion analysis suggested a possible relation to phenanthrene, the bulk of the 1937 product was reduced by the Clemmensen method and the reduction product dehydrogenated with selenium. A high-vacuum distillation of the dehydrogenated material yielded a white crystalline product which was very deliquescent and was insoluble in non-hydrolyzing organic solvents. An analyst in Germany to whom this sublimate was submitted for combustion reported that it contained only traces of organic matter. It was found to be selenium-free and would appear to have been zinc chloride.

To make further study of the chemical nature of the odorous oil would have involved repeating the fractionation with a further supply of maple syrup. This the writers were not in position to do.

Discussion

In describing the products the writers have referred in the main to maple *odour* rather than to maple flavour, since in identification they have relied on smell rather than on taste.

Although the data obtained do not lead to a clear knowledge of the chemical nature of the odorous principle of maple syrup, it is the writers' hope that their method of separating the constituents of the chloroform extract and the isolation, from syrups of two seasons, of a product (or closely related products) in which the characteristic odour develops on standing, may be found of value in future investigation of this problem, to which, in the writers' opinion, no satisfactory solution has yet been found.

Acknowledgments

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THE PREPARATION OF ETHERS[1]

By Philip G. Stevens[2] and Sidney A. V. Deans[3]

Abstract

A new modification of Williamson's ether synthesis, using sodium naphthalene to form the metal alcoholate, has been described, by which the yields and ease of preparation of ethers have been improved.

The most general method for the preparation of ethers from carbinols is still that developed by Williamson (11) over eighty years ago. This consists in treating a metal alcoholate with an alkyl halide, and is the only method which permits the preparation of optically active ethers with the certainty that no Walden Inversion can occur. This method, as usually carried out, has many disadvantages however. One of these is that the yields are seldom greater than 50 to 60% (3), probably due to the fact that the alcoholate formed becomes associated with one or more molecules of the alcohol, which then does not react with the metal (10). This results not only in poor yields, but also in contamination of the ether with the alcohol, necessitating its removal either by repeated distillation from sodium, or by treatment with phthalic anhydride. Another disadvantage is that the higher molecular weight alcohols react even with potassium so sluggishly that often heat must be applied. This sometimes causes racemization as well as the formation of complex products, if two hydrogen atoms are in the α- and β-position to the oxygen atom, as shown by Hückel and Naab (2) with *cis* decalol, and confirmed later by Stevens (9) with methylisopropylcarbinol and 2-ethoxy-3-methyl-butanol-3. A third disadvantage is that the metal may attack the rest of the molecule. To avoid this, Purdie and Irvine (7) used silver oxide and methyl iodide for the methylation of carbohydrates. More recently Kraus and White (4) carried out methylations in true Williamson style by using sodium or potassium in liquid ammonia; and this modification has later been extended to carbohydrates with excellent yields (5). However this method is effectively applicable only with those alcohols or polyhydroxy compounds which are soluble in liquid ammonia, and which form soluble metal salts, and it fails for simple alcohols like hexanol-2.

The writers have now found that almost any alcohol can be very easily converted to its methyl ether with the aid of sodium naphthalene, recently described by Scott, Walker and Hansley (8), as a reagent ideally adapted for the preparation of sodium derivatives of alcohols or other compounds with active hydrogen. The yields are extremely good, and optically active alcohols yield ethers of high rotatory power. The method consists in adding the alcohol to the sodium naphthalene dissolved in an "effective" ether such as glycol dimethyl ether. The formation of the alcoholate is quantitative, and the exact end of the reaction is indicated by the sharp change in colour of the solution. Addition of methyl iodide or methyl sulphate completes the reaction, the products of which are then worked up in the usual way. The only important point is to choose reagents which will not interfere with the isolation of the ether. This is easily accomplished by the use of the proper "effective" ether and aromatic hydrocarbon (8)*. Thus with hexanol-2 and cholesterol, naphthalene is satisfactory, since it can be easily separated from each ether by fractional distillation and steam distillation respectively. With linalool, diphenyl with its higher boiling point is preferred.

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[1] *Manuscript received in original form, June 1, 1939, and as revised, July 17, 1939. Contribution from the Chemical Laboratory, McGill University, Montreal, Canada.*

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The lower molecular weight alcohols gave ethers in less satisfactory yields simply because of manipulative losses and inadequately effective fractionating columns. In these cases the use of dimethyl ether as the solvent might be better, since it is difficult by distillation to separate the methylvinyl ether (b.p. 12 to 14° C.) which is formed by cleavage of the glycol ether (8). Hydroxy compounds with other functional groups, such as ethyl lactate, can also be converted to ethers in this way by merely reversing the process of addition. Here the yields are again lower, but still about as good as those reported by Purdie and Irvine (6) who used silver oxide and methyl iodide.

Experimental

Sodium naphthalene (or diphenyl) is first prepared in glycol dimethyl ether solution according to the directions of Scott, Walker, and Hansley (8). This intensely coloured solution is cooled, and then the alcohol to be etherified is added with mechanical stirring. The sharp colour change from deep green (or blue) to a pale greenish yellow may appear before one equivalent of the alcohol has been added, if some sodium remains undissolved. The addition is then stopped at this point, and the stirring continued until the sodium has practically all dissolved. The titration is then continued until the deep colour again disappears. This occurs now when one equivalent of the alcohol has been added. Either methyl iodide or sulphate is added slowly, keeping the solution below 20° C., and the mixture is allowed to stand overnight.

If the ether is a low boiling one, methyl sulphate is used, and the products can be fractionally distilled directly. If the ether is a high boiling one, methyl iodide is used, the reaction mixture treated with water, and the product extracted with ether, dried, and distilled. In the case of cholesterol, it is necessary to use considerably more glycol ether to maintain a homogeneous solution. After the reaction is over, the entire mixture is steam distilled to remove the naphthalene along with the more volatile materials. The sterol ether is far less volatile than naphthalene, and on cooling, sets to a cake, and is recrystallized from acetone. With ethyl lactate, the sodium naphthalene must be added to the ester to avoid, as much as possible, interaction of excess

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* *The authors' sample of commercial anthracene formed a sodium derivative, but this did not undergo the proper colour change when treated with linalool. This may be due to impurities in the anthracene used.*

sodium naphthalene with the carbonyl group. In this case, as no change of colour indicates the end-point, stoichiometric amounts of each reagent are used, methyl iodide is added, and the products worked up in the usual way. In Table I are assembled all the experimental data.

TABLE I

Alcohol	α_D^{23}	Methyl ether α_D^{23}	B.p., °C.	Yield, %	Reagents used
Propanol-2	—	—	31 (752 mm.)	51	Naphthalene, methyl sulphate
2-Methyl-propanol-2	—	—	54-6 (762 mm.)	55	Naphthalene, methyl sulphate
Hexanol-2	+ 7 1	+ 7 6	115–7 (754 mm.)**	91 5	Naphthalene, methyl iodide
Linalool	−15 2	+14 8	72–5 (10 mm.)†	91 3	Diphenyl, methyl iodide
Cholesterol	—	—	M p. 83–4	87	Naphthalene, methyl iodide
Ethyl lactate	− 6 8	−49 6	139–43 (761 mm.)	60	Naphthalene, methyl iodide

** *This ether after distillation from sodium had the following constants: b.p. 115 to 116° (763 mm.); n_D^{25} 1.3916, d_4^{25} 0 7685. The methoxyl content was 3 5% too high.*

† *On redistillation at 758 mm. the linalool ether boiled at 193.5 to 194°; α_D^{23} + 14.3°; n_D^{25} 1.4481* [*Compare Barbier* (*1*)].

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CALYCANTHINE

IV. A STRUCTURAL FORMULA[1]

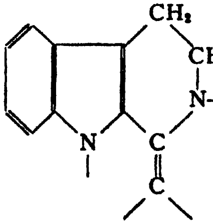
By Richard H. F. Manske[2] and Léo Marion[2]

Abstract

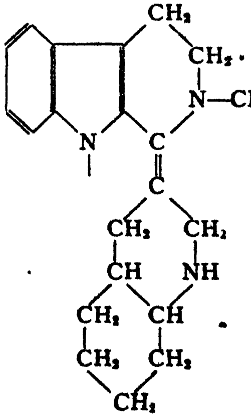
The alkaloid calycanthine ($C_{22}H_{26}N_4$), when degraded with selenium, yields a mixture of norharman, lepidine, skatole, β-ethyl-indole and a base. Heating calycanthine with palladium liberates ammonia. Benzoylation followed by oxidation brings about scission of the molecule into benzoyl-N-methyl-tryptamine and an acidic fragment which contains a benzoylated nitrogen, and another nitrogen, presumably included in a ring. A chemical structure which will account for these results is suggested. On the basis of the suggested formula, the foregoing acidic fragment should contain a hydroquinoline nucleus and it should be possible to dehydrogenate it to quinoline. Such is found to be the case. The formula suggested by Barger, Madinaveitia, and Streuli (1) is discussed.

The alkaloid calycanthine, since its definite characterization by Gordin (2), has been the subject of a number of communications. The most recent is that of Barger, Madinaveitia, and Streuli (1), which contains a structural formula for the alkaloid. We have had this problem under study for several years and are now in a position to suggest for calycanthine a structural formula which differs radically from that published by the authors mentioned above (1).

One of us has shown that N-methyl-tryptamine is obtainable from calycanthine by comparatively mild treatment and has advanced a partial structural formula, (I), representing the carboline-half of the molecule (7). The isolation of quinoline from calycanthine by treatment with hydriodic acid and phosphorus has already been reported by us (8). Now it has been possible to obtain quinoline by an entirely different process, as will be discussed later in this paper. We, therefore, do not believe that quinoline is obtained as a result of deep-seated rearrangements, but that the quinoline nucleus is present in the calycanthine molecule. By combining fragment (I) with quinoline it is possible to arrive at (II). The quinoline is shown attached to the



(I)



(II)

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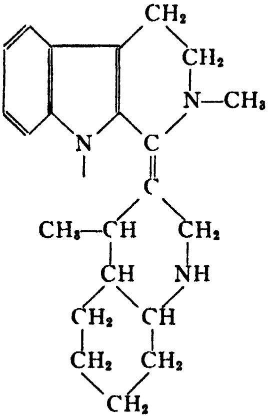
carboline fragment at carbon-atom-2 because that position permits a better understanding of the results of the degradation of the alkaloid with selenium, and the 3- position of the quinoline nucleus is chosen in anticipation of some results which follow.

As already reported (8) the selenium degradation yielded norharman and a base for which we are pleased to retain the designation *calycanine* suggested by Barger *et al.* (1). In a more thorough study of this degradation it has now been found that there is also obtained β-methyl-indole, β-ethyl-indole, and lepidine. The source of the norharman can be regarded as the carboline-half of the molecule since the pyridine ring of the latter cannot become aromatic unless it loses its N-methyl group. Likewise, β-methyl- and β-ethyl-indole are undoubtedly formed from the same fragment. However, the isolation of lepidine makes it possible to extend the partial structural formula (II) to (III).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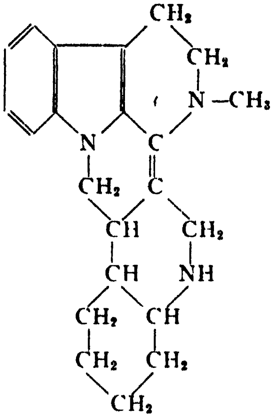
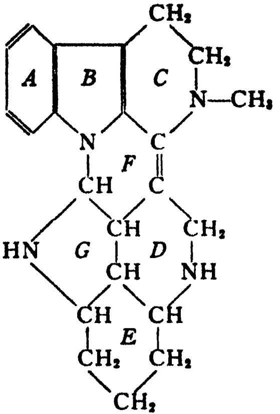
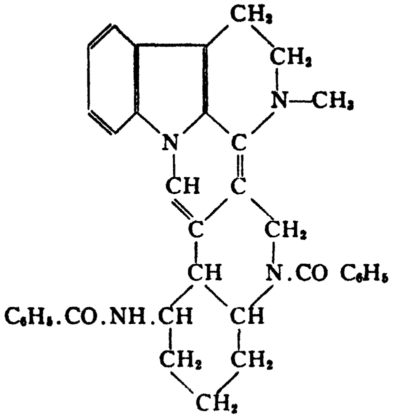

(IV)

Since Barger and his co-workers (1) report the absence of a C-methyl group in calycanthine, it is further possible to link the methyl group of lepidine to the indole nitrogen as in (IV). A search for a 1-methyl-indole derivative in the products of the selenium degradation of calycanthine has proved fruitless. In view of the ease with which a methyl group so situated is eliminated in pyrolytic reactions (5, p. 181; 6), and in view of its presence in the lepidine, it is not thought that the failure to find it in the indole moiety is sufficient evidence that this nitrogen is not substituted in calycanthine. Furthermore, the absence of a C-methyl group in the alkaloid is proof that the methyl group of lepidine must be produced during the degradation. In addition, the fact that, depending on conditions, quinoline or lepidine are obtained as degradation products militates against the occurrence of the methyl group of lepidine as such in calycanthine.

When calycanthine is heated in a stream of nitrogen with palladium, ammonia is obtained. To account for the ease with which ammonia is thus liberated, the fourth nitrogen atom of calycanthine can be included in a reduced pyrrole ring *G* as in (V), thus completing the structural formula of the alkaloid for which the empirical formula $C_{22}H_{26}N_4$ is here accepted rather than the double formula of Gordin.



(V)



(VI)

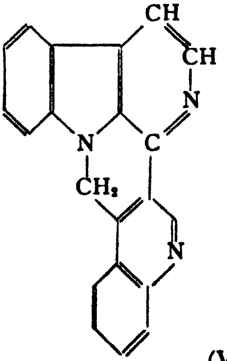
Additional support for the introduction of the fourth N-atom as in ring *G* is to be found in the fact that the N-C bond from rings *B* to *G* is severed easily in the benzoylation experiments (7). As formulated, the nitrogen of ring *G* would probably not be basic to the extent that calycanthine should form a trihydro-halide. It is assumed that it is this nitrogen atom which is so readily eliminated (as methyl-amine) in methylation experiments (1, 4, 8). The introduction of oxygen during these experiments is then readily explicable on the basis of simple hydrolysis. The possibility that the readily eliminated methyl-amine might come from the N-methyl group of ring *C* should not be overlooked, although it is considered that the above-mentioned production of ammonia does not favour such a view.

In the hope of obtaining a clue as to the fate of rings *D* and *E*, a further study of the benzoylation experiments was made. Ultimately, besides benzoyl-N-methyl-tryptamine, an amorphous acid was obtained which contained nitrogen and one or more benzoyl groups. This acid yielded an amphoteric substance when debenzoylated, and quinoline when heated with selenium. The acid is, therefore, probably a largely hydrogenated (5)?-amino-quinoline-3 : 4-dicarboxylic acid in which the nitrogen atoms are lactamised or benzoylated. The nitrogen content supports this assumption. Benzoyl-N-methyl-tryptamine, when similarly treated with selenium, yielded no quinoline.

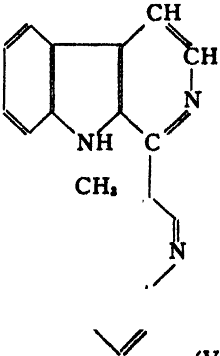
In one benzoylation experiment already reported by one of us (7) a basic substance was obtained, m.p. 235° C. The analytical figures are in excellent agreement with the empirical formula $C_{36}H_{34}O_2N_4$ which, on the basis of structure (V), for calycanthine can be expanded to structure (VI). The steps involved are,—severing of the N-C bond of the five-membered ring *G* by hydrolysis, benzoylation of the nitrogen, elimination of water with the formation of a double bond, as well as benzoylation of the secondary nitrogen of ring *D*.

Calycanthine has not been found to be reducible and is recovered unchanged after treatment with sodium in butyl alcohol. Most double bonds present must presumably form part of aromatic rings. The fact that the double bond of ring *F* in structure (V) was not reduced by this treatment may be attributed to steric hindrance. As already reported (8) calycanthine, when oxidized by Gadamer's method, loses two hydrogen atoms which can be readily added again by reduction. Since the product thus obtained is identical with calycanthine, no stereoisomeric changes appear to be involved, and the two hydrogen atoms concerned are probably removed from the two methylene groups of ring *C*.

As mentioned above, the degradation of calycanthine with selenium yielded a base which Barger and his co-workers (1) have named calycanine. Although we had temporarily (8) suggested the empirical formula $C_{16}H_{10}N_2$ for this base, further examination and analysis of a purer sample shows it to be in good agreement also with $C_{21}H_{13}N_3$ (mol. wt., 307) or $C_{21}H_{15}N_3$ (mol. wt., 309). A determination of the molecular weight gave an average figure of 614 which is twice the required weight, but this might be due to association. Furthermore, calycanine fails to give a colouration with Ehrlich's reagent, indicating that no α- or β- position in the indole nucleus is unsubstituted. On the basis of formula (V) for calycanthine, this degradation product would be expected to be one formed by loss of ammonia and hydrogen In order that ring *C* become aromatic the methyl group must be eliminated from the nitrogen, and thus we arrive at either formula (VII) or (VIII) for calycanine.



(VII)



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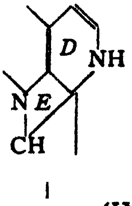
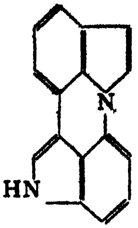


(IX)

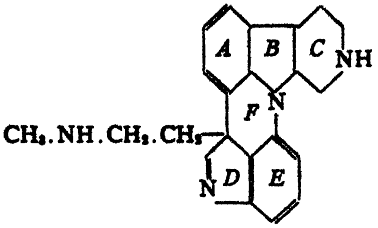
Formula $C_{21}H_{15}N_3$ (VIII) is consonant with the presence of one active hydrogen (1) and contains the methyl group of lepidine, although the tautomeric form of (VII), involving a para link and the wandering of a hydrogen as in (IX), would account for an active hydrogen.

We believe that formula (V) for calycanthine is a reasonable expression for the gross constitution of the alkaloid, although further experimental evidence is necessary to elucidate the detailed structure.

Barger and his co-workers (1) have proposed constitutional formulae for calycanine (X) and calycanthine (XI) which apparently are based upon preconceived notions of biogenesis



(X)



(XI)

and, we believe, a misrepresentation of experimental facts. It is not deemed essential to discuss their formulae in detail, but some errors and inconsistencies deserve mention. The discussion of the biogenesis from two molecules of tryptophane is introduced in their paper by way of the erroneous statement that calycanthine has been isolated from a plant of the family, Compositae, but *Meratia praecox* in common with the genus Calycanthus belongs to the Calycanthaceae family.

We have isolated calycanthine from two other species of *Calycanthus*, namely, *C. occidentalis* Hook. et Arn. which yielded 0.8% of pure alkaloid and from *C. glaucus* Willd. (*C. fertilis* Walt.). For the latter we are indebted to Dr. Alfred Rehder of the Arnold Arboretum, Jamaica Plains, Mass. In both cases the alkaloid was isolated by the procedure used for *C. floridus*, thus it is not considered essential to give experimental details.

In the discussion of their formula (X) for calycanine, Barger *et al.* have overlooked the fact that calycanine does not give Ehrlich's reaction. This negative result indicates that the indole nucleus of calycanine must be substituted in both the α- and β-positions, whereas in formula (X) two α- and one β-carbon atoms are unsubstituted. Furthermore, calycanine is basic and it is highly probable that the compound represented by structure (X) would be neutral.

In support of their formula (XI), the above-mentioned authors (1, p. 513) state that in the course of the reaction yielding N-methyl-tryptamine the bond between the quaternary atom and ring *A* is ruptured (along with that between *B* and *E*), and that the fission is brought about by soda-lime, but not by quick-lime. They conclude that the fission is evidently a hydrolysis rather than a pyrolysis. Yet, in the same paper (1, p. 517) they mention that 30 mg. of N-methyl-tryptamine is obtained per gram of alkaloid when calycanthine is heated with quick-lime at 305° C. for four hours.

The same authors have isolated 2-phenyl-indole as a product of the degradation of benzoyl-calycanthine but have failed to obtain it from calycanthine itself. We also have failed to detect any trace of phenyl-indole among the degradation products of calycanthine and are of the opinion that the phenyl group comes from the introduced benzoyl radical. It is difficult to see how 1-, 2- or 3-phenyl-indole could be derived from the degradation of a structure such as (XI).

Finally, a compound such as (XI) should react with phenyl-isocyanate giving rise to a neutral di-phenylcarbamyl derivative. Calycanthine, as already reported (8), does form a di-phenylcarbamyl derivative, but the latter is basic. In our formula (V) the two secondary nitrogens of rings *D* and *G* would be expected to condense with phenyl-isocyanate and the resulting bisphenylcarbamyl derivative would still be a base owing to the basic nature of the tertiary nitrogen in ring *C*.

Experimental

Degradation of Calycanthine with Selenium

Anhydrous calycanthine* (2 gm.) was heated in a metal bath with selenium (2 gm.) in a stream of nitrogen. The reaction was carried out in a distillation flask connected through a condenser to a receiver. The temperature was gradually brought up to 300° C. and maintained for one-half hour. The flask and the melt, which had set to a hard resin, were crushed together to a powder in a mortar, and the distillate kept separate. Four more runs, each with 2 gm. of calycanthine, were made and the respective products combined.

Isolation of Skatole

The combined distillates from the five runs were dissolved in ether and the ethereal solution was washed with dilute hydrochloric acid, dilute sodium hydroxide, and water. The ethereal solution yielded a neutral brown oil which was distilled. A first fraction, b.p. 115° C./1–1.5 mm., was separated which formed a red picrate, m.p. 166°†. When mixed with skatole picrate (m.p. 178°) it melted at 172°. After recrystallization from absolute ether (1 cc.) it melted at 171° and, in admixture with skatole picrate, at 173.5°.

Isolation of β-Ethylindole

The distillation of the neutral product yielded a second fraction, consisting of a colourless oil, b.p. 125 to 130°/1 mm., wt. 0.262 gm. This was treated with picric acid (0.417 gm.) in ether solution containing a few drops of methanol and the picrate precipitated by the addition of petroleum ether. It was recrystallized once from benzene and once from absolute ether, from which it separated as red needles, m.p. 121° C. The indole was regenerated by shaking an ethereal solution of the picrate repeatedly with aqueous potassium hydroxide and the neutral oil redistilled; b.p. 110°/5 mm. The distillate crystallized immediately in colourless flakes, m.p. 39°, either before or after admixture with β-ethyl-indole. It was reconverted into the picrate, m.p. 120.5°. Admixture with β-ethyl-indole picrate (m.p. 120.5°) failed to depress the melting point.

In this connection, it may be noted here that β-ethyl-indole (m.p. 39 to 40° C.) undergoes on long standing a transformation into a compound, m.p. 81 to 82°, which depresses strongly the melting point of β-ethyl-indole when mixed with it. The transformation product forms a picrate, m.p. 127°, which in admixture with β-ethyl-indole picrate melts at 108°.

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* *In one recrystallization from chloroform-methanol, calycanthine was obtained in needles melting at 214° C. An attempt to recrystallize this yielded the base melting at 245° C. The low-melting form obviously consisted of Gordin's iso-calycanthine (3).*

† *All melting points are corrected.*

Isolation of Lepidine

The hydrochloric acid extract obtained in the course of isolating the indoles from the ether solution of the distillate was basified with strong caustic, which precipitated a granular base. The mixture was shaken with several portions of ether and a small quantity of insoluble product filtered and washed (basic fraction *A*). The ethereal solution yielded a mixture of crystals and oil. It was digested with cold ether which dissolved only the oil. The crystals were combined with basic fraction *A* and the ethereal solution was extracted with dilute hydrochloric acid. The acid solution was filtered through charcoal, basified, and extracted with ether. The mixture of bases obtained from the ether extract was treated with picric acid in methanolic solution. The crystalline picrate (*B*) was filtered off, and the filtrate evaporated to a very small volume, from which a second crystalline picrate was deposited. This, after repeated recrystallization from methanol, melted at 217°. In admixture with lepidine picrate (m.p. 218°) it melted at 217.5°.

The melts obtained from the dehydrogenation with selenium were ground and extracted with ether in Soxhlets. The ethereal extract was washed with dilute hydrochloric acid. The neutral fraction yielded some β-ethyl-indole. The acid solution was basified with strong potassium hydroxide and the precipitated bases were shaken with ether. Some insoluble product was filtered, washed with ether, and combined with basic fraction *A*. The ether solution was then distilled and the residue digested with some cold ether, the insoluble portion being combined with basic fraction *A*. The bases recovered from the ether solution were distilled *in vacuo* and separated into three fractions: I, b.p. 80 to 85°/1 mm.; II, b.p. 100 to 130°/1 mm.; III, b.p. 170 to 180°/1 mm. Fractions I and II when treated with picric acid yielded lepidine picrate, m.p. 217° before and after admixture with an authentic specimen.

Isolation of Norharman

Fraction III crystallized on standing. It was recrystallized from ether from which it separated as small prismatic needles, m.p. 187°. It was converted to a picrate, which melted at 261°, and the free base as well as the picrate did not depress the melting points of 3-carboline (norharman) or its picrate*.

The mother liquor from norharman picrate was combined with the crystalline picrate *B* and decomposed. The bases were again fractionated *in vacuo* and the high-boiling fraction (b.p. 170 to 180°/1 mm.) was converted to the picrate. After a series of fractional crystallizations a picrate was finally obtained which melted at 264 to 265°. The melting point was depressed after admixture with the picrates of norharman, of 1-methyl-3-carboline, and of harman. This base, the solution of which in hydrochloric acid fluoresces, seems to be a carboline, but may not be quite pure.

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* *This isolation and characterization has been detailed already (8), but norharman was then described as 4-carboline. We prefer the more recent nomenclature and refer to it as 3-carboline.*

Isolation of Calycanine

All the basic fractions *A* were combined, dissolved in dilute hydrochloric acid, filtered through charcoal, and precipitated by basifying the solution with strong potassium hydroxide. The base was filtered, washed with water, dried, and dissolved in boiling chloroform. Boiling ethyl alcohol was added to the solution (charcoal) which was then evaporated to a small volume and diluted with boiling ethyl alcohol. The base separated as soft white needles, m.p. 308°. It was sublimed at 210° C./0.001 mm. and recrystallized again from chloroform-ethyl alcohol, m.p. 310°. Calcd. for $C_{21}H_{13}N_3$: C, 82.09; H, 4.24; N, 13.68%.; mol. wt., 307. Found: C, 82.43; 82.70; H, 4.75, 4.54; N, 12.60, 12.68%; NCH_3, negative; mol. wt., 584, 626, 642, 604 (Rast). Calcd. for $C_{21}H_{15}N_3$: C, 81.23; H, 4.85; N, 13.59%; mol. wt., 309.

Treatment of Calycanthine with Palladium

Calycanthine (2 gm.) was mixed with Pd-charcoal catalyst (2 gm.) in a distillation flask carrying a capillary tube, and connected to a condenser reaching into a suction flask. The flask carried a tube dipping into dilute hydrochloric acid. A stream of nitrogen was kept sweeping into the flask through the capillary while the experiment lasted. The mixture was heated to 260° to melt the calycanthine and then maintained at 200 to 210° for five hours. The hydrochloric acid solution in which the gases had been washed was evaporated to dryness, the crystalline residue dissolved in methanol, and a 5% solution of platinic acid (3 cc.) poured into the solution. A brown, amorphous precipitate which separated was filtered and washed with methanol, and the combined filtrate and washings evaporated to about 2 cc., filtered, and evaporated to dryness. The residue was redissolved in a little boiling methanol, and allowed to crystallize on cooling. The lemon-yellow crystals decomposed at 300°, giving off what appeared to be ammonium chloride. Calcd. for $(NH_3)_2 . H_2PtCl_6$: Pt, 43.9%. Found: Pt, 42.9%.

The reaction flask contained some unchanged calycanthine which was mixed with a base the solutions of which in dilute acid were strongly fluorescent. It has not yet been possible to isolate this base in a pure condition.

Benzoylation of Calycanthine

As already reported (7), calycanthine when benzoylated and subsequently oxidized in acetone with potassium permanganate yields benzoyl-N-methyltryptamine. It has now been found that when the manganese dioxide sludge, after filtration and washing with acetone, is digested with boiling water, and filtered, the filtrate when acidified yields a mixture of benzoic acid and another acid which is only sparingly soluble in ether. Use is made of this property to remove the benzoic acid. The acid, which melts at 170 to 174°, could not be crystallized. It contains nitrogen and gives a positive reaction with Ehrlich's reagent on prolonged boiling. Calcd. for $C_{18}H_{18}O_4N_2$: N, 8.59%. Calcd. for $C_{18}H_{20}O_3N_2$: N, 8.77%. Found: N, 9.26, 9.62%.

In order to determine whether this nitrogenous acid contained combined benzoic acid, some was dissolved in methanol (5 cc.) and refluxed 16 hr. with concentrated hydrochloric acid (10 cc.). Water (200 cc.) was added and the cooled liquor extracted with six portions of ether. The combined ether extracts yielded a crystalline residue which was recrystallized from water, m.p. 121.5°. In admixture with an authentic specimen of benzoic acid it melted at 122 to 123°. The aqueous hydrolysis liquor, which had been extracted with ether, was evaporated to a small volume, whereupon a crystalline substance separated which is being further studied.

Isolation of Quinoline

Some of the benzoyl-nitrogenous acid (0.4 gm.) was heated with selenium (5 gm.) in a metal bath, while a stream of nitrogen was kept sweeping through the flask. The temperature was gradually raised to 300° and maintained for one-half hour. The flask and melt were crushed in a mortar, suspended in very dilute potassium hydroxide, and steam distilled. The distillate (150 cc.) was repeatedly extracted with ether, and the combined extracts were washed with two portions of dilute hydrochloric acid. The acid solution was basified with strong potassium hydroxide and extracted with ether. The ether extract yielded a small quantity of oil which was treated with a methanolic solution of picric acid. The crystalline picrate which separated was recrystallized several times from methanol. It melted at 203.5° C. Admixed with an authentic specimen of quinoline picrate, m.p. 204°, the mixture melted at 204°. Some benzoyl-N-methyl-tryptamine (0.5 gm.), when similarly treated with selenium (5 gm.), did not yield quinoline in quantity sufficient for identification.

In an experiment already reported by one of us (7) benzoylated calycanthine was heated for several hours on the steam bath with alcoholic potassium hydroxide; it yielded among neutral and acidic fractions a moderate quantity of a basic substance, which is soluble in aqueous citric acid and crystallizes from alcohol in stout plates, m.p. 235°. It does not give a colour with Ehrlich's reagent. Calcd. for $C_{36}H_{34}O_2N_4$: C, 77.98; H, 6.14; N, 10.11%; mol. wt., 554. Found: C, 77.66, 77.84; H, 6.16, 6.07; N 10.10, 10.07%; mol. wt., 517, 496.

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MICROCHEMICAL TECHNIQUE

III. SEMI-MICRO PREPARATION AND PURIFICATION OF ORGANIC SUBSTANCES[1]

By George F. Wright[2]

Abstract

Several devices convenient in semi-micro preparation and purification of organic substances are described. A modified side-arm test tube is suggested as of general utility in microchemical laboratory technique.

The introduction of quantitative microanalytical methods has facilitated organic chemical research both because of the small amounts required for analysis and because of the time saved in carrying out the semi-micro or micro reactions required for their preparation. The convenience and rapidity of the small-scale procedure has, however, been offset by the fault that quantitative recovery of the products is often difficult, and the significance of the experiment is decidedly lessened thereby. While much of the general microchemical technique is actually older (3) than the quantitative methods of Pregl, the continued rapid advances in the latter art require constant improvement in preparative and purification methods. It seems worth while to report at this time several devices that the author and his co-workers have found useful in manipulation of 1 to 100 mg. of organic substances.

Solubility Tests

A great deal of preliminary information pertaining to solubility, crystallizability, and reactivity may be obtained with the microscope slide using 100 γ of substance not sensitive to moisture or air. If care is taken, this amount suffices, first for successive solubility tests with organic solvents and water, and subsequently for solubilities in acid and alkali. In the solubility and crystallizability tests each solvent is evaporated before the next is added. To effect this evaporation conveniently the slide is placed on the flat top of a large cork borer, mounted vertically, and heated by a microflame (*A*, Fig. 1). This device enables one to heat the slide without undue spreading of the solution over the surface. The test reagents must be applied in small quantities. Suitable containers may be made from glass tubing drawn (Fig. 2) out at one end to a fine thick-walled bent capillary which is at first sealed. The tube is then constricted at the other end, filled with the reagent and then sealed off. The pointed end which remains after sealing is of advantage if the reagent tubes are kept in the ordinary test tube rack. An alternative method of filling, satisfactory with reagents boiling above 50° C., is to seal the lower end of the tube under vacuum and then to break the tip in a beaker of the substance. These tubes have the advantage of delivering clean reagents.

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[1] *Manuscript received June 7, 1939.*
Contribution from the Chemical Laboratory, University of Toronto, Toronto, Canada.

[2] *Assistant Professor of Chemistry, University of Toronto.*

Leakage through the capillary is no greater than through the ordinary glass stopper; however, sensitive or little-used reagents may be preserved by sealing the tip of the capillary with a microflame. The reagent container is manipulated by tipping the tube while it is held lightly in the hand. The body heat imparted by a firmer grasp will then deliver a drop to the appropriate position on the slide. When low boiling solvents, such as ether, are used there is danger that the high vapour pressure forces out more than one drop of the solvent; this difficulty can be obviated by tipping the cold tube so that, when it is tipped back to vertical, one drop is held in the bent juncture between the capillary and the body of the reagent tube. Upon warming the container with the hand this drop may then be forced out on to the slide. It should be pointed out that this method of reagent delivery supplements rather than replaces the use of the micropipette.

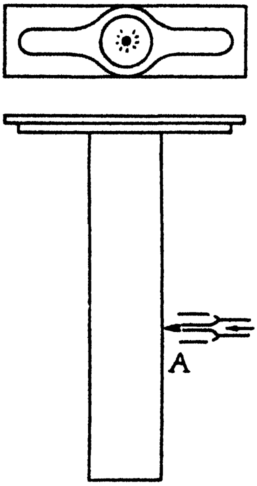

FIG. 1

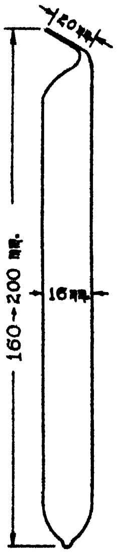

FIG. 2

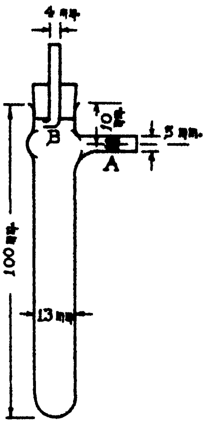

FIG. 3

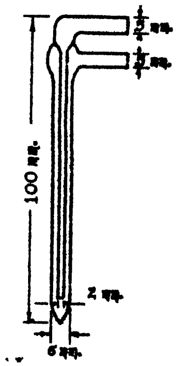

FIG. 4

The determination of solubilities on the microscope slide is necessarily less exact than that outlined by Foulke and Schneider (4) using microcapillaries, but is much more rapid. As a guide toward choice of crystallizing solvent it is more informative; the favourable solvent is obviously that from which the crystalline material separates at the periphery of the spot leaving the impurity at the centre. Magnification, either with the hand glass or the low power microscope, is convenient in ascertaining this solubility difference. Caution must be exercised regarding results with hygroscopic solvents—atmospheric moisture may condense in the evaporating solution and thereby change the characteristic solubility.

The Side-arm Test Tube

This well known piece of apparatus has been modified as shown in Fig. 3 by blowing an enlargement about 5 to 10 mm. below the tip of the flanged 10 by 75, 13 by 100, or 15 by 125 mm. Pyrex test tube and attaching a side-arm to the bulge in such a manner that a trough leads from the tube to the lower side of the arm. The purpose of the alteration is to eliminate contamination of the stopper when liquid is decanted through the side-arm. The tube is of general utility in micromanipulation. Thus, it is used in this laboratory as a reaction vessel, dropping funnel, crystallizing vessel, etc.

For use in crystallization, a plug ot long-fibered cotton wool or fibrous glass (Corning) is tamped into the side-arm as illustrated at *A*, Fig. 3, and a cork (previously boiled or Soxhlet-extracted in ether or acetone to remove soluble constituents) is inserted into the mouth of the tube after it has been equipped with a glass tube pulled off sharply to one side *(B)*. A 3- to 4-ft. length of small-bored rubber tubing is attached to the straight end of the tube *B*. The sample and solvent are placed in the side-arm tube, which is then inclined at an angle with the side-arm up, and is heated in a suitable bath (conveniently over a hot plate) until the solvent is refluxing smoothly. Occasional gentle puffs of air are blown in by mouth through the rubber tubing in order that the solvent will not contaminate tube *B*, but tends, instead, to moisten plug *A*. When the sample is properly dissolved, the hot solution is decanted through the side-arm into a second, previously warmed, test tube. Just enough air pressure is applied by mouth to keep the trough of the crystallizing tube from over-filling, but care should be taken not actually to clear the plug of liquid. A few drops of excess solvent suffices to clean the tube of the soluble constituent. Any undissolved residue remains in the crystallizing tube, from which it may be further extracted with a more suitable solvent. It is evident that this method of crystallization obviates the losses incurred by filtering through a funnel. Because the tube is of uniform bore it is a simple matter to ascertain, by marking the tube with a wax pencil, the minimum amount of solvent or solvents required to effect solution; this makes it possible to record and reproduce the crystallizing conditions. Its disadvantage, namely, loss of solvent, which must be avoided when crystallizing from mixed solvents, may be remedied in the case of slow, difficult solution by replacing the blowing tube *B* with a cold finger (Fig. 4) during the dissolving process. This cold finger, useful when the side-arm test tube is employed as a refluxing reaction flask, is constructed from tubing of 6 mm. outside diameter by blowing an enlargement on a closed tube of this diameter and inserting into it by ring seal a tube of 2 to 3 mm. diameter, the side-arm being subsequently attached.

The use of the side-arm test tube as a reaction vessel and dropping funnel may be illustrated in the characterization of organic halides by means of their Grignard reagents (5). The halide in ether solution is placed in a side-arm test tube equipped with a boiled, dried cork stopper on the arm and a stoppered inlet tube that introduces a slow stream of dry nitrogen. This tube is attached to a second dry side-arm tube which contains the magnesium (Fig. 5). When the system is flushed with nitrogen, the side-arm of the second tube is connected by rubber tubing to the nitrogen manifold; this creates a system isolated under nitrogen atmosphere. A plug of cotton at the nitrogen exit provides a slight positive pressure. The halide is introduced by turning the first tube around the axis of its side-arm so as to effect a dropwise addition to the magnesium, the second tube being maintained at an angle of approximately 45° to insure smooth boiling. Reflux is obtained by cooling the upper part of the tube with a compressed air jet. When addition is complete and reflux has subsided, the prepared reagent is decanted dropwise through a fibrous glass plug (to free it of unreacted magnesium) into a third side-arm test tube, swept out with nitrogen from the manifold and containing the solution of characterizing reagent.

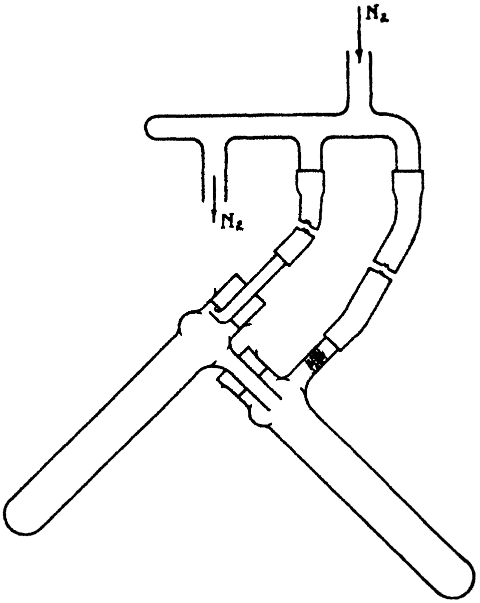

FIG. 5

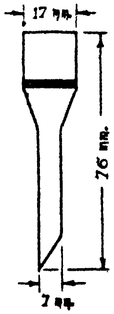

FIG. 6

The Suction Funnel

It is a rule of micromanipulation that, whenever possible, a solution or suspension should not be poured over the lip of a vessel. The sample mentioned above should therefore have been allowed to crystallize in a second side-arm test tube, from which it may be removed by decanting through the arm. There are a number of small-sized suction funnels (Büchner type) available on the market that are suitable to receive this crystalline suspension. The type (Fig. 6) used in this laboratory differs from the conventional porcelain or glass types in that it is made of Pyrex glass with a sealed in porcelain disc. The funnel has been built to accommodate the bevelled, glazed porcelain plates of sizes 22 mm., 14 mm., and 7 mm. diameter. Modifications of this construction have been used for low temperature crystallization apparatus (2) and for continuous ether extractors, in lieu of the sintered glass plates.

The porcelain glass seal is made, especially in the larger sizes, by "tacking" the disc in place at one spot while holding the previously constructed glass part vertically, and then heating a length about ½ inch on either side of the seal with a bunsen burner while an oxygen-gas flame about the size of a darning needle is focused directly on the juncture of porcelain and glass. Such a flame is desirable in order to get a complete wetting or fusion of glass into porcelain, so as to avoid spaces which may become fouled with use. This small sharp flame may be obtained by connecting the two inlet tubes of an ordinary nasal atomizer with gas and oxygen supplies. The supply of oxygen is easily adjusted by means of a needle valve (obtained in the writer's case from an old suction-type automobile windshield wiper) soldered on to the screw top of the atomizer so that it opens directly into the glass bowl. The bowl is then filled with lead shot and plastic cement to furnish stability to this improvised torch, as well as to fill up the dead air space, since the tip will work satisfactorily only with oxygen and not with air. The torch is illustrated in Fig. 7. Its small but very hot flame is useful in such operations as the construction of the ring-seal shown in Fig. 4.

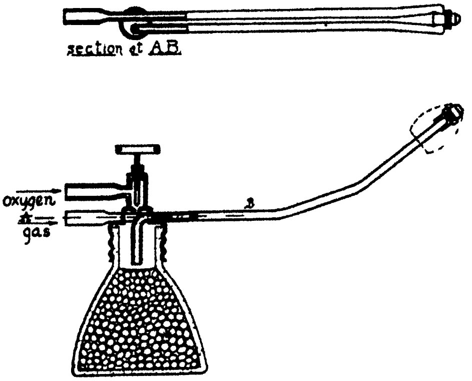

FIG. 7

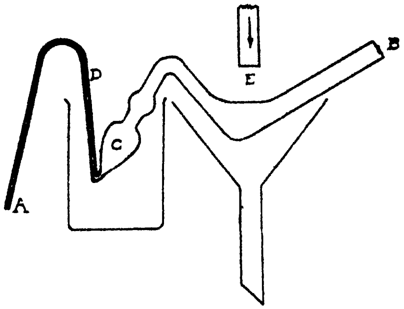

FIG. 8

When the porcelain-glass seal is completed it requires careful annealing because the disc holds its heat so much longer than the glass around it. To test the efficiency of this annealing process, the completed funnel is heated to 100° C. and then chilled in cold water. A properly annealed funnel does not break under such treatment; those that survive the chilling test have been in use for over five years.(*)

The Microdistillation Flask

This method of distillation is an adaption of that developed by Bendetti-Pichler and Schneider (1). The apparatus is constructed from glass tubing

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* *These funnels may be obtained from the firm, Eck and Krebs, 131 West 24th Street, New York, N.Y.*

3 to 7 mm. outside diameter and is bent into the shape illustrated in Fig. 8. The liquid to be distilled is introduced into the pot *C* by dipping the capillary *A* into the liquid and drawing it up by partial vacuum applied at *B*. In the case that the liquid to be distilled is dissolved in a solvent such as ether or benzene, this solvent may be "flashed off" by surrounding the distilling pot *A* with a heated beaker of water or wax, the suction being carefully controlled, conveniently by using an evacuated desiccator as a vacuum chamber. When the substance to be distilled is transferred entirely into the distilling pot, the capillary is sealed off at *D*, with the same mild suction; full vacuum is applied and then released so that the capillary becomes almost filled. A tuft of long-fibered cotton wool is inserted into *B* in such a way that the rubber tubing leading to the vacuum pump holds it so that it cannot be carried along by the gas stream. This is accomplished simply by allowing a few strands of the plug to extend over the outside of tube *B*, though not far enough to cause vacuum leakage at this point. A means of cooling, either of water flowing over the receiver *E* into a funnel, or of dry ice packed around *E* in a shallow dish, is employed. The vacuum required for distillation is then applied and the temperature of the stirred bath is slowly raised until the almost filled capillary empties itself; this represents the initial boiling point of the substance. When fractionation is to be effected, the vacuum is slowly released through the cotton plug, which is then withdrawn and the fraction removed by means of a capillary pipette. The capillary at *D* is broken, resealed under slight suction, and the distillation continued as before. By extending (to 5 cm.) and indenting the column of such an apparatus built from tubing 3 mm. outside diameter, Mr. E. Y. Spencer, of this laboratory, has successfully fractionated 0.1 ml. of liquid into two substances boiling at about 80 and 90° C. under 15 mm. pressure.

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THE REMOVAL OF FLUORINE FROM ALBERTA WATERS[1]

By Osman James Walker[2], Gordon Roy Finlay[3], and Walter Edgar Harris[4]

Abstract

The fluorine removing capacities of a large number of materials have been investigated. Many of these have been found to have little or no effect on the fluorine content of the water, while others have lowered the fluorine content but not enough to prevent mottling of the teeth.

Two materials, specially prepared aluminium oxide and freshly precipitated aluminium phosphate, have been examined and have been found to be equal to, or better than, other materials which have been proposed previously. These two have been compared with activated alumina, tricalcium phosphate, and magnesium oxide, materials reported upon by other writers.

Experiments on these have been carried out using the filtration technique and the stirring and standing technique with good results.

A commercial defluorite unit, containing tricalcium phosphate, supplied by the National Aluminate Corporation, has been tried out at three points in Alberta and found to have a high fluorine removing capacity.

In 1931 Smith and her co-workers (10, 11) and Churchill (4) established the fact that the mottling of teeth is caused by the presence of fluorine in the water supply. It has since been established that the effect on the teeth takes place between the ages of six months and twelve years (5), that is, during the period when the teeth are calcifying within the gums, and that amounts of fluorine (8) over 1 p.p.m.* may lead to mottled enamel. A great deal of thought has been given to the prevention of this tooth defect, as experience has shown that if the teeth are once attacked, the mottling cannot be removed by any method which is now available. It is therefore necessary to prevent mottling in the first place by providing children with a water supply that contains less than 1 p.p.m. of fluorine.

There are two avenues open to residents in many endemic districts. The first method is to switch over from a water high in fluorine to a water low in fluorine (5). This has been done very successfully in a number of localities in the United States. Surveys carried out in the Province of Alberta (13, 14) show that there are some districts where such a change is possible, as the water from shallow wells and streams is generally low in fluorine content even though water from the deep wells is high in this element. In some of these cases it may involve the transportation of water a considerable distance, especially in the dry seasons when shallow wells tend to dry up. In many districts such a step is impossible, as there may not be available an adequate supply of low fluorine, potable water.

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[1] *Manuscript received June 9, 1939.*
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* *p.p.m. is an abbreviation for parts per million parts of water.*

The second method of preventing mottled teeth is to start with a water containing over 1 p.p.m. of fluorine and, by means of some material, lower the fluorine content to less than 1 p.p.m. Since the amount of fluoride involved is so small, precipitation methods are not feasible, as the least soluble fluorides known are soluble to a greater extent than 1 p.p.m. The formation of complex ions containing fluorine may offer some possibilities especially if the resulting compound has a low solubility in water. It may be possible to remove the fluorine from water by a system of anion exchange resembling the base exchange softening of water by zeolites. Of greater importance is probably the removal of fluorides from the water by selective adsorption on the surface of a solid. A combination of one or more of these processes may be the mechanism by which satisfactory removal of fluorine takes place. Since the amount removed is very small it is rather difficult to tell whether one has complex ion formation, anion exchange, or selective adsorption on the surface of a solid.

In order that a material may be used as a fluorine remover it should have a low solubility in water. It should be of proper grain size, say 20 to 40 mesh, so that it has a sufficiently large surface and yet will not remain in the treated water as suspended matter. It should not change the potability of the water. It should be comparatively cheap so that it will be available for country users, many of whom live in districts where crop failures are frequent.

During the last three years, investigators have been busy trying to find methods of removing fluorine from natural waters. The National Aluminate Corporation first used activated alumina (7, 12) for this purpose, but later transferred their attentions to tricalcium phosphate (1, 2) and are now manufacturing commercial units containing this material for fluorine removal. Smith and Smith (9) have recommended the use of crushed bone, while Elvove (6) has suggested magnesium oxide for this purpose. The Permutit Company Limited (3) has patented the use of various dried metallic oxide gels.

Two different techniques have been used in the treatment of waters. The one which has been used by most of the investigators is to pass the water through a column of the remover at such a rate that the fluorine content is lowered below the threshold level of 1 p.p.m. The other scheme is to add a small amount of the solid to a vessel of water, stir, and allow to stand in contact for some time, usually overnight, and then draw off the clear liquid. Fresh water can then be added and the operation repeated until the solid has lost its fluorine removing properties. These two methods have their advantages. In the percolation or filtration method a large amount of the remover may be used at one time, so that large volumes of water may be treated and little supervision is required. When the material has lost its effectiveness it is removed and either discarded or sent to the laboratory to be regenerated. This is the ideal method to be used when the water supply is piped into the home. The other method, sometimes called the spoon and bucket method, can be used most conveniently when the water is taken from the well to the home in barrels or buckets. Only the water for drinking or for cooking need be treated, and, since the amount of remover is very small, it may be discarded after having been used once or twice.

The investigation of fluorine removers by the present authors was begun in 1937 prior to the appearance of many of the papers which have been mentioned. Both procedures have been used. A large number of materials have been examined, many of which have little or no fluorine removing power. Others have been found to remove fluorine but not enough to lower the fluorine content below 1 p.p.m. Several have been found to be excellent for the purpose in addition to those reported by other investigators. It was also found that the fluorine removing capacity depended on whether the material was freshly prepared or had been taken from stock bottles, and also on the method of drying and the temperature of drying.

The water used in most of the investigations was that delivered from the taps in Edmonton, the source of the supply being the North Saskatchewan River. To this was added sufficient sodium fluoride to bring the fluorine concentration up to a definite amount, usually 4 p.p.m., but other concentrations were used in some experiments. The composition of Edmonton city water (in p.p.m.) in September, 1937, was as follows:

Total dissolved solids at 105° C.	200
$SO_4^{=}$	30
Cl^-	4
Bicarbonate alkalinity (temporary hardness)	110
Carbonate alkalinity	0
Total hardness (soap method)	152
F^-	0.2
pH	8.2

During the winter months the mineral content may be as much as 70% higher than the values shown here. A number of tests have also been conducted on high fluorine Alberta waters, but these have been limited in number owing to difficulties in transporting sufficient quantities to the University laboratories.

The following materials were found to have no fluorine removing properties: titanium oxide, titanium hydroxide, zinc oxide, copper hydroxide, manganese dioxide, hydrated manganese dioxide, various silica gels, bentonite, zirconium silicate, beryl, ilmenite, a limy subsoil, copper sulphide, flowers of sulphur, calcium oxalate, calcium oleate, trimagnesium ortho-phosphate, barium carbonate, barium sulphate, magnesium oxychloride, chromium borate, Portland cement, permutite, boracite, and limestone.

Materials with a low capacity for the removal of fluorine were basic ferric carbonate, magnesium ammonium phosphate, aluminium oxalate, powdered aluminium, and various hydrated ferric oxides precipitated on asbestos and dehydrated at different temperatures. In no test with these materials was the fluorine content of the water lowered to a value less than 1 p.p.m. However, the aluminium oxalate, which was ineffective in earlier runs, showed a fair capacity when further amounts of water were treated.

Removal of fluorides was observed with magnesium oxide as used by Elvove (6), and with activated alumina (8) and tricalcium phosphate (12) supplied by the National Aluminate Corporation. In addition, results were obtained with tricalcium phosphate supplied from various sources, hydrated aluminium oxide given different heat treatments, a mixture of aluminium oxide and calcium carbonate, and freshly prepared aluminium phosphate. The best results were obtained using aluminium oxide dried at 81° C., and aluminium phosphate.

In the first series of experiments the materials used were different forms of alumina which had been dried under different conditions. The description of these fluorine removers is as follows. For Run 1, the aluminium oxide had been dried at red heat; for Run 2 the aluminium oxide had been dried at 81° C. for four hours; for Run 3, the drying had been carried out at room temperature; while for Run 4, aluminium hydroxide had been precipitated on shredded filter paper, air dried for two days, and then heated for 12 hr. at 190° C. For Run 5, activated alumina (Defluorite *A*) supplied by the National Aluminate Corporation, was used.

In these experiments the materials were placed to a height of about 50 cm. in tubes about 2.0 cm. in diameter. The water used contained 8 p.p.m. of fluorine. Gravity flow was used in all runs.

There was a considerable variation in specific gravity of these materials and thus a considerable variation in the weights used. The amounts of materials in Runs 1, 2, 3, 4, and 5 were 7.4, 7.4, 7.1, 78, and 200 gm. respectively.

Results are shown in Table I. The curves in Fig. 1 are calculated from

TABLE I

REMOVAL OF FLUORINE BY ALUMINIUM OXIDE

*Volume of water treated, litres	F^- content of effluent, p.p.m.				
	Run 1	Run 2	Run 3	Run 4	Run 5
0.5	0.45	0.1	0.1	0.3	0.7
1.0	0.35	0.1	0.15		0.1
1.5	3.0	0.1	0.1	0.2	0.2
2.0		0.3	0.1	0.3	0.3
2.5	7.0	1.3	1.0	0.5	0.4
3.0	8.0	2.0	2.0		1.6
3.5	8.0		3.7	0.2	1.4
4.0			5.0	0.1	1.2
4.5			7.5	0.6	1.5
5.0				0.5	3.0
6.0				0.7	4.5
7.0				0.7	5.0
8.0				1.1	5.5
10.0				3.0	
11.0				4.5	
12.0				7.5	

* *For Runs 4 and 5 multiply volumes by 10.*

Table I in such a manner that abscissae represent litres of water treated by 100 gm. of material and the ordinates represent the fluorine content of the effluent. Litres per 100 gm. of material is roughly the same as gallons per pound.

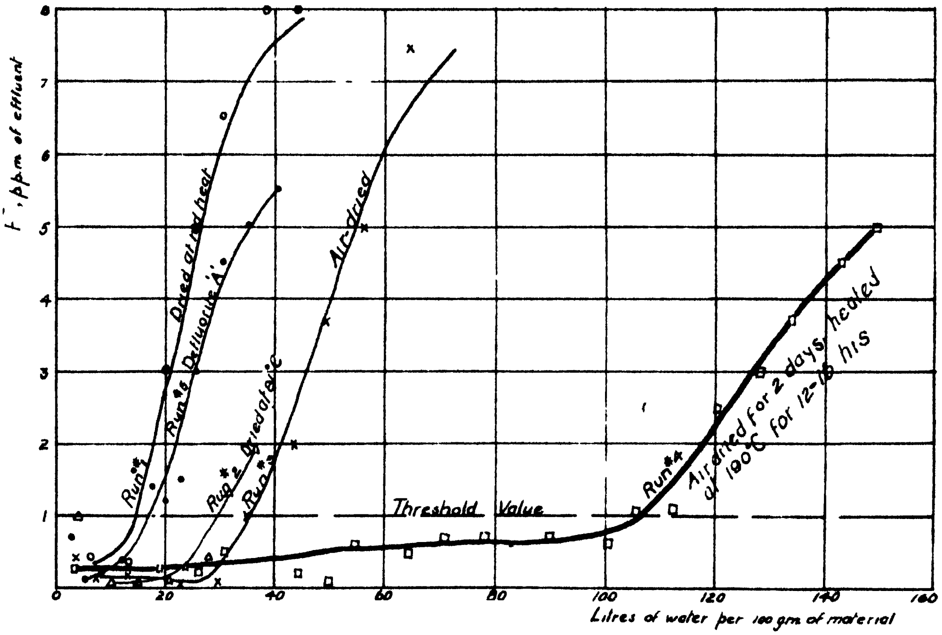

FIG. 1. *Removal of* F^- *by alumina.*

From Fig. 1 it can be seen that of the five forms of alumina only that used in Run 4 removed sufficient fluorine to justify its use as a fluorine remover. It will be noted that 100 gm. of this particular alumina is capable of lowering the fluorine content of more than 100 litres from 8 p.p.m. to less than 1 p.p.m.

Most of the tests on fluorine removing materials were conducted using the second technique in which a quantity of the material was added to a measured quantity of high fluoride water, stirred thoroughly, and allowed to stand overnight. The treated water was then drawn off and analyzed. A fresh portion of the water was added and treated in the same manner. The procedure was repeated until the fluorine removing power was lost. This technique was favoured because it is more easily followed by the householder in the country and in the small village.

As in the previous series of experiments, good results were obtained from hydrated alumina treated in different ways, from a mixture of co-precipitated alumina and calcium carbonate, and from aluminium phosphate from several sources. For comparison purposes runs were made using magnesium oxide and the commercial preparations of the National Aluminate Corporation, activated alumina here designated as Defluorite *A*, and tricalcium phosphate designated as Defluorite *B*. In addition, experiments have been carried out on tricalcium phosphate from other sources.

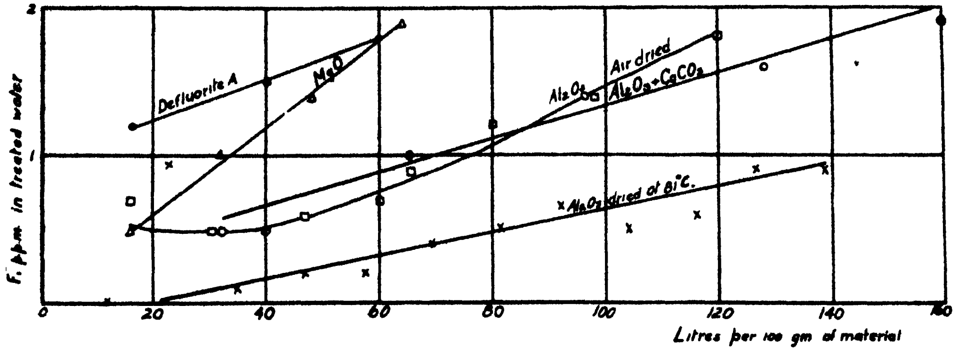

FIG. 2. *Removal of F^- by oxides.*

Table II contains the data obtained and these have been expressed graphically in Figs. 2 and 3. Fig. 2 contains results on oxides, Fig. 3 results on phosphates. In all instances the fluorine content of the water used was 4 p.p.m. except where alumina dried at 81° C. was used, in which case the fluorine content was 3.8 p.p.m. The weight of material used each time was 5 gm. except with alumina dried at 81° C., when 13 gm. was used.

TABLE II

REMOVAL OF FLUORINE BY OXIDES AND PHOSPHATES

F^- content of treated water in p.p.m.

Volume of water, litres	Al_2O_3			$Ca_3(PO_4)_2$		MgO	$AlPO_4$			Al_2O_3 + $CaCO_3$
	Defluorite *A*	Dried at		Defluorite *B*	Baker		Fresh	Baker	Schuchardt	
		Room temp.	81° C.*							
0.8	1.2	0.7		0.0	2.2	0.5	0.2	1.0		
1.5			0							
1.6		0.5		0.6	1.0	1.0	0.2	1.2	0.9	0.5
2.0	1.5	0.5								
2.4		0.6			1.8	1.4	0.6	1.3		
3.0	1.8	0.7	1.0							
3.2		0.9		0.8	2.0	1.9	0.6	2.0	1.8	1.0
4.0		1.2		1.4	1.8		0.8			
4.5			0.1							
4.8		1.4		1.4			1.3		2.6	1.4
5.6				1.3			1.6			
6.0		1.8	0.2							
6.4				1.4			1.3			1.6
7.2				1.8			1.2			
7.5			0.2							
8.0				2.0			1.2			1.9
9.0			0.4							
9.6							1.4			
10.5			0.5							
11.2							2.0			
12.0			0.65							
13.5			0.5							
15.0			0.6							
16.5			0.9							
18.0			0.9							

* *Used water containing 3.8 p.p.m.F^-.*

It will be noticed that in some cases the first result is higher than later results. The materials seem to require a soaking before they begin to behave normally. From Fig. 2 it can be seen that Defluorite *A* is not so effective as some of the other forms of alumina. The magnesium oxide used was not nearly so effective as the variety used by Elvove (6). The alumina dried at 81° C. is the same as that used in the filtration technique, the results of which are shown in Fig. 1. It is much more effective in these experiments probably because of the fact that it was quite gelatinous and did not allow the water to run through very readily in the first series. The mixture of alumina and calcium carbonate is not as effective as some of the other forms. In it, only the alumina is active, as the calcium carbonate has been shown to be incapable of removing fluorides. This mixture was used to obtain a more granular product.

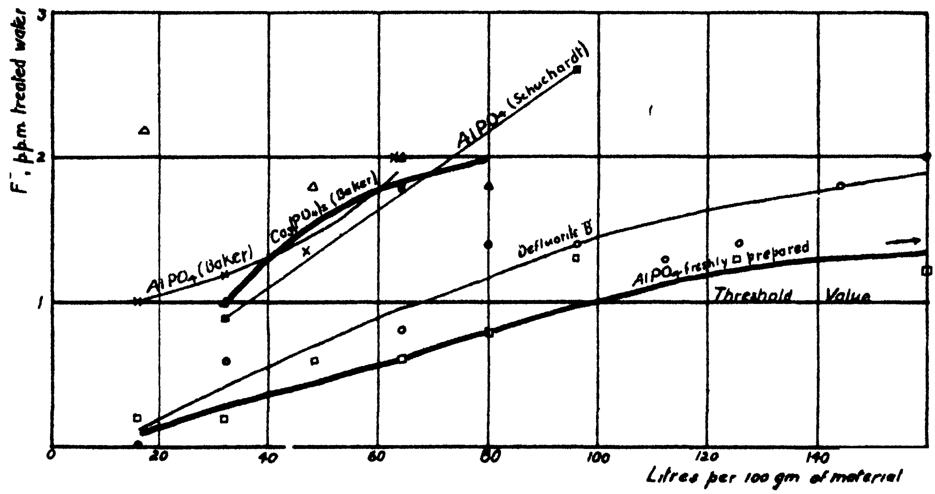

FIG. 3. *Removal of F^- by phosphates.*

From the results in Fig. 3 it can be seen that the effectiveness of freshly prepared aluminium phosphate is of the same order as that of Defluorite *B* and much greater than that of the samples manufactured by Baker and Schuchardt. The capacity of Defluorite *B* is lower with this technique than when the filtration method is used. The aluminium phosphate was prepared by treating aluminium nitrate and monosodium phosphate with ammonium hydroxide, filtering, and then drying in the air. It contained about 45% water. The effectiveness increased somewhat on standing.

From the values given here it can be seen that 1 lb. of alumina dried at 81° C. can lower the fluorine content of 140 gal. of water containing 4 p.p.m. to less than 1 p.p.m., while 1 lb. of the prepared aluminium phosphate can do the same for about 100 gallons. Air dried alumina has also been found to be effective.

It is presumed that if these three preparations remove fluorine from North Saskatchewan River water to which fluorides have been added then they should also be effective with high fluorine natural waters. It is hoped that these materials will be tried out in the near future in areas where mottled teeth is prevalent.

It has been possible, however, to place in service at three points in the province a defluorite unit (1), containing tricalcium phosphate (Defluorite *B*), all of which was kindly furnished by the National Aluminate Corporation. This unit consists of a closed vessel with an inlet tube at the top and an outlet tube at the bottom and contains 10 lb. of 20 to 40 mesh tricalcium phosphate. The material when exhausted may be removed and revivified by sodium hydroxide solution followed by hydrochloric acid or carbon dioxide gas. The unit may be operated under pressure or by gravity. When it is operated under pressure the rate of flow of the water should be no greater than 3 gal. per min. When it is operated by gravity the amount of water treated is about 0.5 gal. per min.

The unit containing fresh material was operated quite satisfactorily at Gwynne, Olds, and Granum. The composition of these waters is given in Table III.

TABLE III

COMPOSITION OF WATER USED IN FLUORINE REMOVAL EXPERIMENTS, IN P.P.M.

——	Gwynne	Olds	Granum
Total solids at 105° C.	964	880	1128
Loss in ignition	212	180	136
SO_4^-	11	15	342
Cl^-	70	8.6	65
Bicarbonate alkalinity	485	660	325
Carbonate alkalinity	138	6	56
Total hardness (soap method)	0	18	22
$PO_4^{\equiv}$ as P_2O_5	4		0.5
F^-	1.1	3.3	4.4
pH	9.3	8.3	8.55

These three waters are characteristic of many of the high fluorine Alberta waters. In general, it has been found that the pH of such waters is greater than 8.3. Many of them contain considerable quantities of sodium bicarbonate as do the three whose values are shown here.

When defluorite units were operated at these points, a sample of the original water and treated samples taken during the progress of the test were collected and analyzed for fluorine content. In most of these cases it was necessary to conduct the analyses in such a way that phosphates would not interfere, as they were present in the treated water, coming partly from the calcium phosphate.

Table IV contains the results of these experiments.

TABLE IV

REMOVAL OF FLUORIDES BY DEFLUORITE UNIT

—	F^- determined, p.p.m.		
	Gwynne	Olds	Granum
Rate of flow	3 qt. per min.	Fairly rapid	Slow and intermittent
Untreated water	1.1	3 3	4.4
At 50 gal. point			0.1
100 "		0	0.2
200 "	0	0.2	0.2
250 "		0.2	0
300 "		0.4	0.2
350 "		0.5	0.3
400 "	0	0.6	0.2
450 "		0.6	0.2
600 "	0.4	1.0	
800 "	0.4		
1000 "	0.6		
1200 "	0.7		
1400 "	0 6		
1500 "	0.8		

The operation of the units may be looked upon as satisfactory. The materials used at Gwynne and Olds had practically reached the state of exhaustion and had to be regenerated. The unit operated at Granum was very satisfactory and undoubtedly could have been used for treating considerably more of this water.

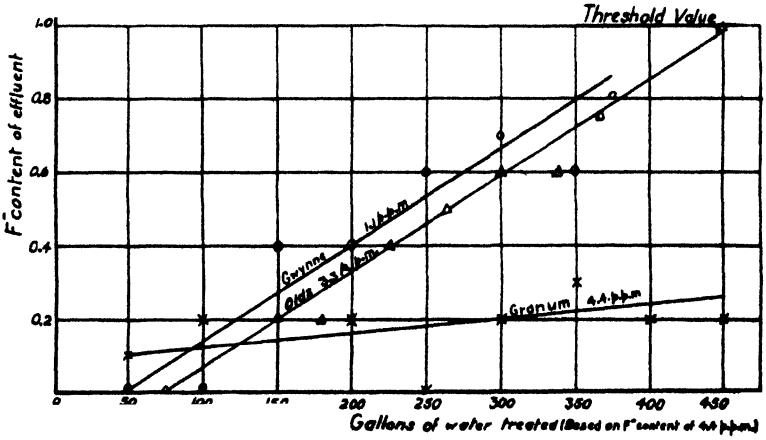

FIG. 4. *Removal of F^- by defluorite unit* [$Ca_3(PO_4)_2$].

The behaviour of these units is expressed graphically in Fig. 4. In this figure the graphs are based on equal amounts of fluorine which passed through the unit. The comparison has been made by taking into account the number of gallons of Gwynne and Olds waters equivalent in fluorine content to 1 gal. of Granum water. For example, 400 gal. of Gwynne water shown in Table IV appears in Fig. 4 as 100 gal. and 400 gal. of Olds water appears as 300 gal. This figure shows that the performance of the unit at Granum was much better than at the other two points. The longer time of contact in the unit may account for the better results.

Summary

It seems clear that the problem of preventing mottled teeth has reached a point where adequate preventives are now available. In addition to those proposed by others, different forms of hydrated alumina as well as aluminium phosphate are added to the list. It is necessary, however, to make careful surveys of endemic regions in order to advise the residents regarding the best methods of prevention. Such surveys have been made in some regions but owing to lack of funds have not yet been made in the province of Alberta. Since persons from other provinces have been observed suffering from mottled enamel it may be a much wider national problem than many suspect.

Acknowledgment

The authors would like to thank the National Aluminate Corporation for the gift of two complete defluorite units.

NOTE—The methods used to determine fluorine in the work described above will form the subject matter of a subsequent paper.

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DETERMINATION OF THE SPECIFIC SURFACE OF FIBROUS MATERIALS[1]

By E. J. Wiggins[2], W. B. Campbell[3], and O. Maass[4]

Abstract

The Kozeny equation relating specific surface and permeability of a bed of unconsolidated particles has been shown to be applicable to fibrous materials such as glass, wool, and celanese. The diameters of the constituent fibre may be as small as 0.0006 cm., while their ratio of length to diameter may be indefinitely large. Uniformity of size or of packing is not essential.

Introduction

Although fibre surface area is of the greatest importance in most applications of fibrous materials, as yet no satisfactory method is available for its determination. Direct microscopic methods, in addition to tediousness, have obvious objections. The physical form of the fibre is usually so complex as to preclude accurate measurement of the area of any individual, and likewise in most cases the individual fibres in a sample differ considerably in dimensions; this necessitates the measurement of a large number of specimens in order to obtain a fair approximation to the average specific surface. The method to be presented, involving determination of permeability to liquids of a bed of the material, has been investigated with a view to solving this problem.

The basic principles result from an equation relating specific surface and permeability deduced by J. Kozeny (4) from purely theoretical considerations. Carman (2) has stated the equation in a serviceable form and developed experimental procedures for its application. This paper and a preceding one (1) by the same author provide an excellent review of the theoretical considerations of the problem.

The permeability, k, is defined as the linear rate of flow of liquid through the bed under unit hydraulic gradient.

$$K = \frac{Q}{A} \cdot \frac{L}{h} \tag{1}$$

Where Q = quantity of liquid flowing through bed in unit time;
A = area of cross section of bed;
L = depth of bed;
h = head of liquid in consistent units.

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Contribution from the Department of Physical Chemistry, McGill University, Montreal, Canada. This investigation was carried out in co-operation with the Forest Products Laboratories of Canada, Montreal, and formed part of the research program of that institution.

[2] *Holder of a scholarship from the Pulp and Paper Association at the time of the investigation.*

[3] *Technical Adviser, Canadian Pulp and Paper Association.*

[4] *Macdonald Professor of Physical Chemistry, McGill University.*

Equation (1) is merely a statement of D'Arcy's law, namely, that the linear rate of flow through a porous medium is proportional to the pressure gradient across the bed.

The relation between permeability and specific surface, termed the "Kozeny equation", is given by Carman as follows:—

$$S_0 = 14\sqrt{\frac{1}{K\nu}\,\frac{\epsilon^3}{(1-\epsilon)^2}} \tag{2}$$

Where S_0 = "specific surface" = surface area per unit volume of actual material comprising the bed;

K = permeability as before;

ν = kinematic viscosity $= \dfrac{\text{absolute viscosity}}{\text{density of liquid}}$;

ϵ = "porosity" = free volume in bed expressed as a fraction of the total volume.

Note $S_0 = \dfrac{S}{1-\epsilon}$, where S = surface area per unit volume of bed.

Equation (2) is valid only for the condition of viscous or streamline flow, the criterion being that

$$\frac{Q}{A\nu S} < 2\,. \tag{3}$$

However, this condition is amply fulfilled for all cases encountered in the present investigation. The great value of the Kozeny equation, if substantiated, as a means of determining fibre area lies in its validity for any shape of particle, and in the ability of the term $\dfrac{\epsilon^3}{(1-\epsilon)^2}$ to correct for various degrees of porosity of the bed. An extensive investigation of the effects of variation of particle size, porosity of bed and liquid viscosity was conducted by Carman, the experimental results indicating that the equation expresses the variables in correct relation. Variation of particle shape and the mixing of various sizes provided further evidence in its favour. However, the most extreme departure from spherical form was represented by crimped wire of 0.03 cm. diameter and straight length 0.57 cm., so that further experimental study was necessary before applying the equation with assurance to particles of the type found in ordinary fibrous materials.

Experimental Procedure

The apparatus employed for the permeability determination is illustrated in Fig. 1, and is a modified form of that used by Carman.

The bed of particles is packed in the tube A and rests on a 20-mesh copper gauze B, which is in turn supported by a spiral of thin sheet copper C. The tube A is of as uniform cross section as possible, and is calibrated by filling both limbs with water, closing D, and weighing the water run out for a series of levels in A. A fixed head of liquid is maintained on the bed by a common

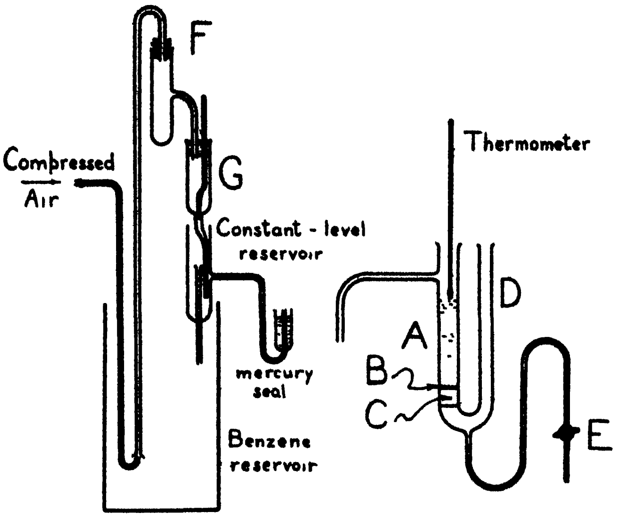

FIG. 1.

overflow type, constant-level device. Water and benzene were used in the investigations, the latter requiring a mercury seal for the connection between permeability tube and constant level reservoir, as shown at the left of Fig. 1. The overflowing benzene is recirculated by means of an air-lift, the intervening reservoirs *F* and *G* serving to smooth the flow and allow entrained air to escape.

The rate of flow of liquid is controlled by means of stopcock *E*, and the corresponding pressure drop across the bed obtained from the difference of liquid levels in tubes *A* and *D*. A minor scale, graduated in 1 mm. divisions, is used to read the liquid level in *D*, the level in *A* being transferred to the same scale by means of a sliding index; this scale is also used to measure the depth of the bed. The rate of flow is obtained by weighing the liquid passing through the bed during a definite time interval. Density and viscosity data for the liquids used were obtained from standard tables. The apparatus was not thermostatically controlled, but the constancy of the ambient temperature was such as to enable reading the temperature of the liquid to 0 1° C., well within the required limits.

The bed is prepared by filling the permeability tube with the liquid to be circulated, and introducing a weighed quantity of the solid material with constant stirring. Considerable difficulty was encountered in obtaining a bed free from entrained air, especially with the more fibrous particles; in such cases the side arms were closed and suction applied to the bed.

The densities of the various materials used were determined by displacement of benzene or water in a pycnometer flask. The volumes of solids were calculated from the weight and density of the particles, and the total volume of the bed from its depth and cross section; from the two values the porosity was obtained.

Experimental Results

1. Preliminary measurements were made with beds of screen-classified sand, similar to those used by Carman. Since the actual specific surface of the sand particles was not known, these determinations served mainly to show the constancy of the calculated values with different liquid viscosities and depths of bed. It was also possible to note how closely the variation of specific surface from a fraction of particles of one size to another compared with that calculated from the ratios of average particle diameters.

Typical results are listed in Table I.

TABLE I

Size range	Liquid	Average particle diameter, cm.	$K\nu$	ϵ	S_0, cm.^{2}/cm.^{3}	S_0d
−10 +14 mesh	Water	0.141	1.163×10^{-2}	0.440	67.9	9.58
−20 +28	Water	0711	4.19×10^{-3}	0.430	116.8	8.30
−28 +35	Water	0503	2.15×10^{-3}	0.443	160.8	8.10
−28 +35	Benzene	0503	2.58×10^{-3}	0.456	157.0	7.90
−35 +48	Water	0356	0.928×10^{-3}	0.436	235	8.38
−48 +65	Water	0252	0.561×10^{-3}	0.430	293	7.37

If the shapes of the sand grains were identical over the entire size range, the specific surface should vary inversely as the average diameter, and thus the product S_0d, where d = diameter of particle, would be a constant. The departure actually shown in the upper and lower fractions was probably an indication of variation in average shape, microscopic examination indeed showing the larger particles to be nearly spherical and the smaller sizes more complex.

2. To obtain particles in a form resembling that of fibres, heated glass rod was pulled out to an approximate diameter of 0.04 cm. The resulting strands were sorted, cut into 8 mm. lengths, and the diameters of a random sample of 100 measured with a micrometer. A weighed quantity of the glass was then packed into the tube A, and the permeability of the bed to water determined.

Experimental data were as follows—

Permeability $K\nu$ (average of 10 runs) $= 4.78 \times 10^{-2}$

Porosity $\epsilon = 0.685$

Calculated $S_0 = 115$ cm.^{2}/cm.^{3}

Average diameter of strands = 0.0407 cm. (extreme variation = 0.0275 to 0.0525 cm.)

Ratio of length to diameter $L/d = 20$

Actual $S_0 = 101$ cm.^{2}/cm.^{3} Ratio of calculated value to measured value = 1.14.

3. The permeability to water of a bed of No. 38 enameled copper wire (5 mm. lengths) was determined as before.

Permeability $K\nu$ (average of 22 runs) $= 2.14 \times 10^{-2}$
Porosity $\epsilon = 0.830$
Calculated $S_0 = 433$ cm.^{2}/cm.^{3}
Diameter of wire $= 0.01017$ cm. L/d ratio $= 50$
Actual $S_0 = 394$ cm.^{2}/cm.^{3} Ratio of calculated value to measured value $= 1.10$

4. To obtain greater departure from sphericity and more closely simulate the physical form of actual fibres, beds of ordinary glass wool were investigated. Permeability determination were made with both water and benzene on beds consisting of glass wool in 1.5 and 6 mm. lengths. Since rod-like particles of this kind would show a tendency to orientation during the packing process, beds were prepared both by random packing and by allowing the fibres to settle after suspension in the liquid with mechanical agitation. Any appreciable effect should then be evident from a comparison of the two results.

Paraffin-block sections were prepared from a sample of the glass wool, and the cross sectional area and perimeter calculated from microscopic measurements. The cross section proving to be of hour glass form, the outline was plotted on graph paper for this purpose.

TABLE II

Fibre length, mm.	L/d ratio	Liquid	$K\nu$	ϵ	S_0 cm.^{2}/cm.^{3}	Remarks	$\frac{\text{Calculated value}}{\text{Measured value}}$
6	200	Benzene	4.70×10^{-3}	0.910	1965	Random packing	0.894
6	200	Water	2.95×10^{-3}	0.895	2090	Random packing	0.950
6	200	Water	1.106×10^{-3}	0.846	2130	Natural settling	0.968
$1\frac{1}{2}$	50	Water	1.294×10^{-3}	0.857	2165	Natural settling	0.985

Specific surface calculated from microscopic examination—2200 cm.^{2}/cm.^{3} (for a uniform fibre S_0 = ratio of perimeter to cross sectional area).

5. To obtain still greater ratios of length to diameter and smaller actual diameters, Corning "fibreglass" No. 008 was employed. Three different types of bed were used, the fibreglass being first cut into 1.5 mm. or 8 to 10 mm. lengths, or merely packed into the tubes without preliminary treatment. Permeability determinations were made with both water and benzene. The fibre cross sectional area and perimeter were determined from microscopic measurements as with the larger glass wool.

6. To test the validity of the equation when a considerable size variation existed in the bed, approximately equal quantities of fibreglass and glass wool, each in 1.5 mm. lengths, were thoroughly mixed.

TABLE III

Fibre length, mm.	Approx. L/d ratio	Liquid	$K\nu$	ϵ	S_0	Calculated value / Measured value
1½	200	Benzene	2.32×10^{-4}	0 885	6660	0.95
8–10	1000	Benzene	$4\ 08 \times 10^{-4}$	0 919	7540	1.1
Continuous		Benzene	5.30×10^{-4}	0 928	7560	1.1
Continuous		Water	4.97×10^{-4}	0 930	8070	1.2

Actual specific surface = 7×10^3 *cm.*^{2}*/cm.*^{3}

Results of permeability measurements with water on the mixture were as follows:—

Permeability $K\nu$ (average of 14 runs) = 7.62×10^{-4}

Porosity ϵ = 0.909

Calculated S_0 = 4830 cm.^{2}/cm.^{3}

Actual S_0 (calculated from relative quantities and specific surfaces of fibreglass and glass wool) = 4710 cm.^{2}/cm.^{3} Ratio of calculated value to measured value = 1.03

7. Celanese yarn was cut into 5 mm. lengths, the filaments were unravelled by rubbing, and the resulting material was formed into a bed; the permeability to benzene was determined in the usual manner. The cross sectional areas and perimeters of the filaments were estimated from microscopic measurements with the aid of drawings of the outline. However, owing to the complex form, the calculated surface area could not be relied on to be of greater accuracy than ±20%.

The apparent density of the fibres was obtained by simple displacement of benzene in a pycnometer flask. This determination was carried out with the celanese in equilibrium with room humidity, as were also the permeability and area measurements. While the atmospheric humidity was undoubtedly subject to some fluctuation, it was assumed that the variation of moisture content from this cause would not introduce serious error. It was further assumed in determining the superficial density by displacement of benzene that none of this liquid would be adsorbed by the celanese.

TABLE IV

Run	Average $K\nu$	ϵ	S_0, cm.^{2}/cm.^{3}	Calculated value / Measured value
1	1.574×10^{-3}	0.898	2950	1.0
2	1.749×10^{-3}	0.904	2990	1.0

Actual S_0 = $3.0 \pm 0.5 \times 10^3$ *cm.*^{2}*/cm.*^{3}

Discussion

In the preceding section, substantial agreement is shown between the values of specific surface as calculated from permeability determinations and from the geometry of the particle. In the size ranges of most interest for future practical application, namely fibreglass and celanese, the agreement is within the accuracy of the determination of actual surface area.

The presence of more than one size of particle, at least when in approximately equal quantities, does not affect the applicability of the method. Furthermore, non-uniform packing of the bed does not seem to be a troublesome factor. This is striking in view of the wide variation of the $\frac{\epsilon^3}{(1-\epsilon)^2}$ term in the Kozeny equation for relatively small changes in ϵ, from which it might be thought that the effect of the more closely packed portions of the bed on the permeability would not be counterbalanced by the looser sections.

The nature of the particle surface in contact with the liquid is found to exert no influence on the permeability for such widely different materials as copper, glass, and celanese; also for both polar and non-polar liquids as water and benzene.

The results of this investigation indicate that the Kozeny equation may be confidently applied to the determination of the specific surface of materials of the type mentioned, with indefinitely large L/d ratios, and with fibre diameters as small as 0.0006 cm. Size mixtures are admissible at least within the range 5 : 1 and where the relative quantities are not widely different. In a recent paper (3) Carman has shown that satisfactory results are obtainable from a mixture of very wide size variation, so that it appears probable that the Kozeny equation would be equally applicable to fibre mixtures.

Further investigation is necessary in order to extend the study to non-rigid materials of more complex structure, such as natural cellulose fibres. A further complication is here introduced in that swelling effects are of the greatest importance. This work is being undertaken at the present time with the ultimate object of determining the surface area of wood pulp fibres, and possibly correlating with this the results from the commercial "freeness tester".

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A MODIFIED PROCEDURE FOR THE DETERMINATION OF CAROTENE IN SILAGE[1]

By A. C. Neish[2], W. D. McFarlane[3], and W. A. Brechin[4]

Abstract

The pigments in silage which have been formed from xanthophyll by acids and which interfere in the determination of carotene have been separated by chromatographic methods and found to exhibit solubilities intermediate between those of carotene and xanthophyll. A method based on the partition coefficient of carotene and the interfering pigments in the system hexane-benzyl alcohol was found to give reliable estimates of carotene.

Introduction

It has frequently been observed that silage made from freshly cut green herbage when analyzed by the conventional methods may appear to contain more carotene than was found in the original plant material (3, 4, 6–9, 11). Quackenbush, Steenbock, and Peterson (8) have recently made a thorough study, by chromatographic analysis, of the pigments present in acid treated alfalfa silage. Five new pigments were identified which were not present in the untreated forage and three of these were shown to have been formed from xanthophyll by the action of acid, and to closely resemble carotene in their solubilities.

The writers have analyzed samples of silage for their carotene and xanthophyll content with the results shown in Table I. The determinations were made by the method of Guilbert (1); a 10 gm. sample of the fresh silage or a 1 gm. sample of the dried material was used and the final colour intensity measurements were made with an Evelyn photoelectric colorimeter (440 filter). The clover silage was prepared from freshly cut red and alsike clover—alfalfa aftermath which had flowered and which was found to contain 0.026 mg. of carotene per gm. of dry matter. The fall rye, cut when about fifteen inches high, analyzed 0.238 mg. of carotene per gm. dry matter. Compared with these values for the original herbage, the results in Table I indicate an increase in carotene due to ensiling the clover and a decrease in the case of fall rye. The carotene analyses of the herbage were carried out with vacuum dried samples, and the results may therefore be low. Under the conditions employed, carotene was definitely destroyed during the ensiling of fall rye.

Drying the silage *in vacuo* for 12 hr. at 90° C. results in a very marked increase in the apparent carotene content and a corresponding decrease in xanthophyll. This observation was made use of in the experiments to be described below. A simple procedure is described for separating carotene from the interfering pigments formed from xanthophyll, thus making possible the determination of carotene in silage.

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TABLE I

CAROTENE AND XANTHOPHYLL DETERMINATIONS ON SILAGE, SHOWING THE EFFECT OF DRYING THE SAMPLE FOR 12 HR. *in vacuo* AT 90° C.

(Results expressed in milligrams per gram dry matter)

Sample	pH	Fresh			Dried		
		Carotene	Xanthophyll	*c/x* Ratio	Carotene	Xanthophyll	*c/x* Ratio
Clover silage·							
(1) No treatment	5 18	0 054	0 388	0 139	0 201	0 240	0 840
(2) Phosphoric acid*	4 37	040	366	110	255	180	1 419
(3) Molasses**	4 40	042	374	112	225	167	1 349
Fall rye silage·							
(4) Phosphoric acid	4 27	163	668	244	471	300	1 570
(5) Molasses	4 40	137	615	233	375	260	1 445

**9 litres of 32 5% phosphoric acid was added to 1000 lb of herbage.*

*** 40 lb. of molasses dissolved in 20 lb. of water was added to 1000 lb. of herbage.*

Experimental

Large samples of fresh and dried fall rye silage, representing equal amounts of dry matter, were refluxed with a 20% solution of potassium hydroxide in ethyl alcohol for one hour, and the carotenoid pigments extracted with petrol ether. The petrol ether extract was washed with water and the xanthophyll next extracted by shaking with 92% (by volume) ethyl alcohol, three washings gave a distinct separation. The petrol ether fraction was concentrated *in vacuo* and put through a column of magnesia and siliceous earth according to the method of Strain (10). The carotene was washed through the column with petrol ether, whereas the other pigments were tenaciously adsorbed in two bands at the top of the column; the upper was greenish-yellow and the lower orange-yellow. The latter could be separated into two orange-yellow adsorption bands by washing slowly with a mixture of ethanol (1% by volume) and petrol ether. These findings are in agreement with the observations of Quackenbush *et al.* (8). A much larger quantity of these pigments was contained in the chromatogram from the heat treated silage. It would appear also that the presence of these "*X*" pigments in plant material is not confined to silage since they were found to be present, in considerable amounts, in a chromatogram of the carotenoid pigments extracted from a sample of fall-rye herbage which had been dried *in vacuo*.

After the carotene had been removed the remaining pigments were eluted with absolute ethanol; these are referred to below as "*X*" pigment. A comparison was made of the properties of a solution of crystalline β-carotene and of the pigment solutions prepared from silage to find some difference on which a method for the determination of carotene in the presence of "*X*" pigment might be based. No significant difference was observed in the colour reaction with antimony trichloride or in the rate of oxidation with benzoyl peroxide.

However, considerable difference was noted in the phase distribution of carotene and "*X*" pigment between petrol ether and the following solvents:—benzyl alcohol, allyl alcohol, furfuryl alcohol, phenyl ethyl alcohol, and dimethyl phthalate. In each case, carotene remains chiefly in the petrol ether whereas the greater part of the "*X*" pigment goes into the other solvent, the latter therefore showing solubilities intermediate between those of carotene and xanthophyll.

Benzyl alcohol was considered the best solvent to use because it gave a good separation and is more readily procurable and less expensive than the other solvents. Petrol ether was replaced by hexane, which has a more definite composition. Because of the incomplete separation of the pigments it was considered advisable to make one phase separation and calculate the amount of carotene present from experimental data on its distribution in a hexane-benzyl alcohol system. Benzyl alcohol dissolves hexane, the miscibility depending on temperature. If 8 ml. of benzyl alcohol and 12 ml. of hexane are mixed at 20° C., each phase at equilibrium has a volume of 10 ml. For convenience therefore these volumes of the two solvents were employed.

METHOD FOR THE DETERMINATION OF CAROTENE, XANTHOPHYLL AND "*X*" PIGMENT IN SILAGE

The silage should be properly sampled as soon as it is taken from the silo and the analyses carried out without delay, because the carotene content diminishes on exposure of the material to the air.

A 10 gm. sample is placed in a 300 ml. Florence flask, 30 ml. of 50% aqueous potassium hydroxide and 60 ml. of 95% ethanol are added, and the mixture is refluxed for one hour on a water bath. The material is transferred to a 250 ml. centrifuge bottle, and the flask rinsed out with water; 50 ml. of ethyl ether (peroxide-free) is added; the contents of the stoppered bottle shaken for two or three minutes, and, after centrifuging, the ether layer is suctioned off into a 300 ml. separatory funnel. Four more extractions with ethyl ether are made using two 50 ml. and two 30 ml. portions. The combined ether extracts are washed five times with water; the ether is distilled off *in vacuo* and 70 ml. of hexane introduced into the flask before the vacuum is released. If the carotene content only is to be determined, hexane may be substituted for ethyl ether; thus the distillation may be avoided. The solution is finally transferred to the separatory funnel using 70 ml. of 92% (by volume) ethanol. The xanthophyll is washed from the hexane solution with 92% (by volume) ethanol, four washings usually giving complete extraction. The washings are combined in a 250 ml. volumetric flask, diluted to volume, and the xanthophyll content is determined by photoelectric colorimetry, the results being expressed in terms of carotene by reference to a graph obtained with solutions of pure carotene.

The hexane solution is transferred to a 100 ml. volumetric flask, diluted to volume, and its carotene and "*X*" pigment content determined as follows:—

A portion (12 ml.) of the hexane solution is placed in a colorimeter tube; the colour intensity is measured with an Evelyn photoelectric colorimeter (440 filter) and the pigment concentration expressed in terms of the carotene reference graph. To the hexane solution is added 8 ml. of benzyl alcohol, the mixture shaken thoroughly, and placed in a water bath at 20° C. until a clear separation of the two phases occurs. The pigment present in the hexane phase is then determined using the colorimeter attachment described by Parker and Griffin (5), which made it unnecessary to remove the hexane phase from the benzyl alcohol phase.

If T represents the total carotenoid in the system and H represents the carotenoid in the hexane phase, then $T - H$ will approximate the "X" pigment content of the system because of the low solubility of the "X" pigment in hexane (see Fig. 1). Knowing the value $(T - H)$ a correction can be made for the amount of "X" pigment in H by reference to Fig 1, which shows the distribution of "X" pigment in the system. Then H − ("X" present in hexane phase) gives the true carotene content of the hexane phase. The carotene content of the system can now be read from Fig. 1, which shows the distribution of carotene in the system. The true value for "X" pigment is the difference between the total carotenoid and carotene values.

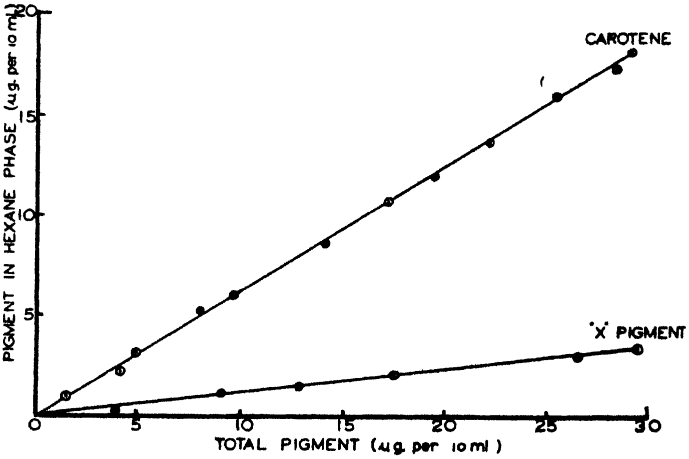

FIG. 1. *Phase distribution of carotene and "X" pigments in the system benzyl-alcohol-hexane.*

Discussion

Analysis of mixtures of carotene and "X" pigment (Table II) showed that fairly accurate values are obtained for the carotene content of the system, provided that the "X" pigment : carotene ratio does not exceed 2, a value which is not likely to be found in silage. The five samples of silage referred to in Table I were analyzed for carotene, xanthophyll, and "X" pigment by this procedure. The vacuum-dried samples were likewise analyzed. Thus an indication was afforded of the accuracy with which carotene could be estimated in the presence of a relatively large amount of "*X*" pigment.

TABLE II

SHOWING THE RECOVERY OF CAROTENE FROM MIXTURES OF CAROTENE AND "*X*" PIGMENT AS CALCULATED FROM THE PHASE DISTRIBUTION

Total carotenoids, µg.	Ratio ("*X*" pigment/ carotene)	Carotene, µg.	
		Present	Found
33.6	0.41	23.8	23.8
22.8	0.63	14.0	13.6
15.8	0.71	9.2	9.4
39.6	0.76	22.5	22.8
29.6	0.95	15.2	15.0
26.4	1.13	12.4	12.0
9.6	2.20	3.0	2.9
19.2	2.20	6.0	6.6
16.2	3.88	3.4	4.6

From the results summarized in Table III it will be seen that in all these samples of silage the amount of "*X*" pigments is relatively small, representing approximately 10% of the carotene content. The validity of the method proposed for determining carotene in the presence of the acid decomposition products of xanthophyll is supported by these results. Drying *in vacuo* resulted in a marked destruction of xanthophyll, whereas carotene was remarkably stable. Only about 35% of the xanthophyll lost by drying was recovered as "*X*" pigment. This may be due in part to the fact that the concentration of all the pigments is expressed in terms of the absorption by carotene of light of wave-lengths approximating 440 mu. The absorption coefficient of "*X*" pigment may be much less than carotene. A sample of silage No. 5 was heated in a sealed glass tube for 24 hr. at 90° C. In this way heating was accomplished without drying. The results of the analysis of this material were practically identical with those of the vacuum-dried sample.

TABLE III

CAROTENE, XANTHOPHYLL, AND "*X*" PIGMENT CONTENT OF SILAGE

(Results expressed in micrograms per gram dry matter)

Sample	Xanthophyll		Carotene		"*X*" pigment	
	Fresh	Dried	Fresh	Dried	Fresh	Dried
1	366	288	23	23	3	38
2	358	238	24	26	3	32
3	367	258	31	33	6	47
4	525	379	57	55	2	34
5	483	392	44	50	5	45

Acknowledgments

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Note added July 24, 1939

Since the completion of this work, Hegsted, Porter, and Peterson (2) have published a method for the determination of the carotene content of silage in which diacetone is employed to remove the pigments other than carotene. Some carotene is lost in the diacetone extract, as it is on extraction with benzyl alcohol, an objection which caused us to discard the use of repeated extractions with this solvent in favour of a single phase separation. They claim however that the loss of carotene in the diacetone extract is offset by the amount of non-carotene pigment which remains in the carotene fraction. We intend to compare this method with our own procedure at the first opportunity.

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CO-ORDINATION COMPOUNDS OF 1 : 3-DIAMINOISOPROPANOL[1]

By J. G. Breckenridge[2] and J. W. R. Hodgins[3]

Abstract

1 : 3-Diaminoisopropanol combines with cobaltous salts to give a series of cobaltic co-ordination compounds, which had been previously prepared by the use of roseo-cobaltic salts. The base has also been found to give crystalline co-ordination compounds with cupric, silver, and zinc salts.

The co-ordination compounds of 1 : 3-diaminoisopropanol have been investigated by Mann (6), who obtained stable compounds with cobaltic cobalt and nickel. Since that time the interesting series of co-ordination compounds of the ethanolamines with cobaltous cobalt were investigated by Hieber and Levy (4, 5), Duff and Steer (1), Garelli and Tettamanzi (2), and Tettamanzi and Carli (8). As stable co-ordination compounds of cobaltous cobalt with aliphatic amines were desired for another purpose, it was thought possible that compounds similar to those with the ethanolamines might be prepared from diaminopropanol. This proved not to be the case, the compound obtained by interaction of the diamine with cobaltous chloride being similar to that obtained by Mann (6) from the diamine and roseo-cobaltic chloride. It was evident that spontaneous oxidation had taken place, this phenomenon being a characteristic of co-ordinated cobaltous salts.

However, it was not immediately apparent that the two compounds were identical, since the crystals were dissimilar, and on drying over phosphorus pentoxide *in vacuo* at 100° C. the writers' compound lost water corresponding to $2H_2O$. The compound prepared by Mann (6) had not been dried in this manner, and thus there was no record of this behaviour. The structure assigned by Mann to his series of compounds was (I), and in view of the apparent distinction between the two, the writers thought it possible that their series of compounds might contain cobaltous cobalt, and would then be represented by (II). Elementary analysis could not decide the point, since the two formulae differ by only one hydrogen atom.

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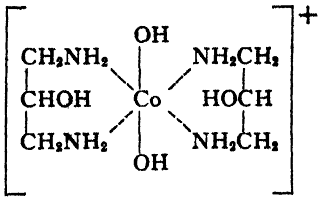
I



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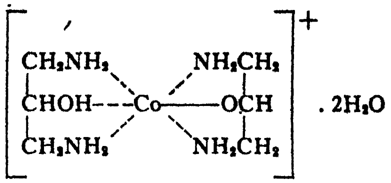
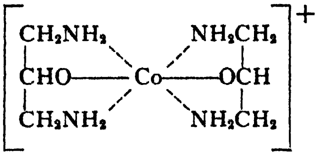


III



On re-investigation of Mann's compound, it also was found to lose two molecules of water on drying as described, to give a product of appearance identical to the writers'. Also, a series of compounds prepared from cobaltous salts and the diamine all lost exactly two molecules of water on drying, and since it is unlikely that they would all contain two molecules of water of crystallization (especially the thiocyanate), another explanation was sought.

It will be seen that in a compound of formula I, two molecules of water may be lost from the two "free" hydroxyl groups and the hydrogens of the alcoholic hydroxyl groups, giving a product of formula III. In this case, all six co-ordination positions of the cobalt atom are taken up by bridged groups, but it is difficult to imagine any other structure. The stereochemistry of this ion will be precisely similar to that of cobalt and α,β,γ-triaminopropane, described by Mann and Pope (7), when only one of the three theoretically possible isomerides could be isolated.

There remained to be explained the different crystalline forms of the compounds prepared by means of the two methods. The compound obtained from roseo-cobaltic chloride crystallized in small needles, whereas the compound from cobaltous chloride appeared as monoclinic prisms. It was thought at first that this difference might be due to *(a)* dimorphism, or *(b) cis-trans* isomerism, since in (I) the two "free" hydroxyl groups may occupy adjacent or opposite corners of the octahedron. However, a crystallographic examination (reported in the Experimental section) showed that the crystals differed only in habit, and were otherwise identical. It was thus evident that the compounds prepared by means of different methods were the same, but the transformation of (I) into (III) on drying was thought sufficiently novel to be worth while placing on record.

Metals other than cobalt were also investigated, copper, silver, and zinc giving crystalline products. The compounds with cupric salts were deep violet, and were of the general formula $[\mathrm{Cu\ dap_2}]X_2$, with the copper atom in the normal 4–co-ordinated state. An unstable crystalline silver salt was isolated, having the formula $AgNO_3 \cdot \mathrm{dap}$. The salts formed with the zinc halides were in a few cases well crystallized, but analysis produced no definite results for a simple compound, and they could not be recrystallized without altering their empirical formula.

Experimental

1 : 3-Diaminoisopropanol (Eastman Kodak Co. Practical grade) was purified either through the hydrochloride, as in the purification of triethanolamine by Germann and Knight (3), or by one distillation *in vacuo* in an all-glass apparatus (b.p. 113° C. at 4 mm., 132° at 14 mm.). It was stored in a desiccator over soda-lime.

Cobalt Compounds—General Formula $[(C_3H_9N_2O)_2Co]X$

Ten grams of $CoCl_2 . 6H_2O$ (or the equivalent of anhydrous salt) in 200 cc. 95% ethanol was added to 20 gm. of base (3 moles + excess) in 100 cc. 95% ethanol, and the mixture shaken. An exothermic reaction took place, and a reddish oil appeared, which crystallized on further shaking. The product was filtered, washed with ethanol, and recrystallized from water, giving well formed, clear red crystals in nearly theoretical yield. On drying over phosphorus pentoxide *in vacuo* at 100° C. water was lost; this left salmon-pink crystals with a bronze lustre, which broke down very readily to a powder.

Similar compounds were prepared from cobaltous bromide, iodide, and nitrate, the thiocyanate by treating a water solution of the iodide with potassium thiocyanate, and the camphor-10-sulphonate and the α-bromocamphor-π-sulphonate by interaction of the iodide and the silver salt of the camphor sulphonic acid. All these compounds were similar in appearance to the cobalt chloride compound, and behaved in the same manner on drying.

The analytical figures for the dehydrated compounds are given in Table I.

A sample prepared from the base and roseo-cobaltic chloride, as described by Mann (6), lost water corresponding to $2H_2O$ on drying:—calcd., 11.7%;

TABLE I

Compound	Mol. wt.		Cobalt, %	Halogen, %	Nitrogen, %	Loss on drying, %
Chloride	272.7	Calcd. Found	21.6 21.2	13.0 12.9	20.5 20.2	11.7 11.5
Bromide	317.1	Calcd. Found	— —	25.2 24.9	17.7 17.6	10.2 9.9
Iodide	364.1	Calcd. Found	16.2 16.4	34.8 34.6	15.4 15.3	9.0 9.2
Thiocyanate	295.3	Calcd. Found	— —	— —	23.7 23.4	10.9 11.1
Nitrate	299.2	Calcd. Found	— —	— —	23.4 23.6	10.8 10.6
d-Camphor-10-sulphonate	468.3	Calcd. Found	— —	— —	11.9 11.8	7.2 7.2
d-α-Bromocamphor-π-sulphonate	547.2	Calcd. Found	— —	— —	10.2 10.1	6.2 6.3

found, 11.6%. In all respects except the appearance of the crystals this was similar to the compound prepared directly from cobaltous chloride.

Specimens of the crystals of the chloride prepared by the two methods were submitted to Dr. M. A. Peacock of the Department of Mineralogy for crystallographic examination, and he reports as follows—

"Monoclinic: $a : b : c = 1.134 : 1 : 0.861$; $\beta = 110° 27'$

Forms: $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $q\{\bar{1}11\}$.

Twin planes: (100) on some crystals.

Measured angles:

	Sample *A*		Sample *B*	
Face	φ	ρ	φ	ρ
$c(001)$	90° 00′	20° 27′	90° 00′	20° 25′
$m(110)$	43° 12′	90° 00′	43° 10′	90° 00′
$q(\bar{1}11)$	−26° 53′	43° 31′	−24° 39′	43° 57′

"The crystals from Samples *A* and *B* give practically the same angles, but they differ in habit. Sample *A* (prepared from cobaltous chloride) are prismatic with large *m*, narrow *a* and *b*, *q* larger than *c*, and always twinned on (100). Sample *B* (prepared from roseo-cobaltic chloride) are single individuals with large *m*, narrow *a* and *b*, large *c*, and very narrow *q*, which gives very poor signals."

Copper Compounds—General Formula $CuX_2 . (C_3H_{10}N_2O)_2$

Cupric chloride (1 mole) in 95% ethanol added to excess base in ethanol gave a dark blue solution, which in a few minutes deposited a blue oil. This crystallized on shaking, giving a lilac-coloured microcrystalline compound, very soluble in water, and only slightly soluble in ethanol. The product was recrystallized from 90% ethanol; this gave deep violet crystals, which decomposed on heating at 181° C. The yield was nearly theoretical. A similar product was prepared from copper bromide. Copper nitrate gave a product of the same appearance, but with a decomposition point of 160° C., after softening at 135° C. There was no loss of weight on drying the above-mentioned compounds over phosphorus pentoxide *in vacuo* at 100° C. The analytical figures are given in Table II.

TABLE II

Compound	Mol. wt.		Copper, %	Halogen, %	Nitrogen, %
Chloride	314.7	Calcd. Found	20.2 20.3	22.5 22.3	17.8 17.6
Bromide	403.6	Calcd. Found	15.8 16.1	39.6 39.6	13.9 13.7
Nitrate	367.8	Calcd. Found	— —	— —	22.8 22.9

Silver Compound

Silver nitrate (3 gm.) in 80 cc. of 95% ethanol was added gradually to 1.6 gm. of base in 50 cc. of 95% ethanol, with stirring and cooling. On standing, the milky solution deposited small white needles, which were filtered and washed with ethanol. The compound was unstable, and began to decompose within a few hours. Calcd. for $C_3H_{10}N_2O . AgNO_3 . 0.5H_2O$: Ag, 40.1, N, 15.6%. Found: Ag, 40.2, 40.1; N, 15.3, 15.6%. When absolute ethanol was used as the reaction medium, crystallization was very slow.

Zinc Compounds

Zinc chloride in 95% ethanol was mixed with excess base in ethanol and the mixture allowed to stand. An oil appeared which crystallized very slowly, giving hard clear white crystals. These were filtered, washed, and dried. Analysis gave the following: Zn, 17.7; Cl, 14.4; N, 17.0%. This does not correspond to any simple formula for the product. The product was recrystallized from water (very soluble), and the microcrystalline product gave the following figures: Zn, 34.4, 34.3; Cl, 18.8, 18.8%. Calcd. for $C_3H_9N_2O$. ZnCl: Zn, 34.4; Cl, 18.7%. These figures remained unchanged when the compound was again recrystallized from water, but when washed with alcohol the percentage of chlorine became 30.7%, and the compound did not appear to be homogeneous.

Similar results were obtained with the product from zinc iodide and the base—the analytical figures were altered on recrystallization, and it seemed likely that hydrolysis was taking place.

Acknowledgments

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THE ACTIVITY OF WATER IN SULPHURIC ACID SOLUTIONS AT 25° C. BY THE ISOPIESTIC METHOD[1]

By H. Sheffer[2], A. A. Janis[3], and J. B. Ferguson[4]

Abstract

The activities of water in aqueous solutions of sodium chloride and of sulphuric acid have been compared by the isopiestic method at 25° C. over a range of molalities extending up to that of the saturated salt solution. The apparatus, which was of the Sinclair type, proved to be as efficient as any yet devised. The results remove the uncertainties that previously existed in regard to the position of the m_1/m_2 curve and give a qualitative indication of the second dissociation of sulphuric acid. The calculated activities agree with the best available data. The isopiestic standard chosen by Janis and Ferguson has been confirmed over the whole molality range.

Introduction

In an earlier paper, a sodium chloride standard for isopiestic measurements was proposed by Janis and Ferguson (7). Comparisons of solutions of sodium and of potassium chlorides at 25°, 30°, and 35° C. confirmed the selections made by them over the possible range of molalities. An attempt was made to confirm the selections at the higher molalities by a study of sulphuric acid solutions. The confirmation was as good as the available data on the acid would warrant, but there were certain discrepancies between these results and those of Scatchard, Hamer, and Wood (8) whose paper appeared just as the writers' paper was being sent to press. The results of these other investigators were not themselves entirely concordant, and it appeared desirable to re-investigate this acid over a wide range of molalities. This was especially so since there was a possibility that new vapour tension measurements on the stronger acid solutions might be available in the near future and the present uncertainty in our knowledge of these solutions thereby removed.

Experimental

The apparatus and procedure were essentially those described by Janis and Ferguson for the small silver dishes. A 6 in. desiccator containing a 5½ in. copper block with depressions for four dishes proved more efficient than the larger apparatus previously used. The block rested on a layer of paraffin wax which held it in position and also thermally lagged it.

The dishes were placed directly in the depressions in the block without the use of any liquid in the latter. Dishes with similar solutions were placed in diagonally opposite positions. The evacuation was carried out carefully to

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prevent spattering, the formation of large bubbles being avoided. Evaporation losses were controlled by a careful re-fitting of the lids when necessary by the manufacturer and by weighing the worst dishes first. They did not exceed 0.0005 gm. per dish. All weights were corrected to *in vacuo*. Whenever the weight was large enough, the dried salt was weighed directly into the cleaned dishes. In all other cases, known solutions of salt and of acid were either weighed in the dishes or added to the dishes from weight burettes.

The apparatus was tested by the use of four dilute solutions, the maximum difference in the molalities being about 4%. After two weeks the final molalities of these brines were 0.08999, 0.09012, 0.09014, and 0.09015. The writers' experience seems to show that the evacuation materially aids in the attainment of equilibrium and undoubtedly is a disturbing factor in rate experiments. However, it is unreasonable to suppose that an agreement in final molalities like that just given could arise from simple pumping, with the attendant disturbance of temperature conditions. The experiments lasted from 24 hr. for the stronger solutions to two weeks for those at and below 0.1 *m*. Twenty-four hours was not sufficient for experiments in which the salt solutions contained solid salt, owing, no doubt, to the fact that in this case several processes were taking place simultaneously.

In all experiments the sodium chloride was from the same lot as that used by Janis and Ferguson, and the water was conductivity water. Salt solutions were made up by weight from salt carefully dried at 600° C. The original acid solutions from which weight dilutions were made were themselves analyzed by weight titration using sodium carbonate and phenolphthalein. The procedure was essentially that of Hillebrand and Lundell (5). The carbonate was prepared from the recrystallized bicarbonate by heating to constant weight in an atmosphere of carbon dioxide at 600° C. Four samples of acid were compared. These are respectively: *(a)*, B.D.H. Analar; *(b)*, Acid *(a)* redistilled by Janis; *(c)*, Acid *(a)* redistilled by Janis and Sheffer; and *(d)*, Grasselli c.p. acid redistilled by Shankman (3). The distillations were carried out in an all-glass apparatus at a reduced pressure in a stream of nitrogen, and the middle third portion was taken. Acid *(b)* was used in the earlier work and Acid *(c)* in the final measurements. The isopiestic molalities were respectively: *(a)* 4.379; *(b)* 4.381; *(c)* 4.371; and *(d)* 4.370. The difference between the molality of *(b)* and of *(c)* was confirmed by two rather extensive series of isopiestic measurements only the second of which is reported in this paper. There must have been some slight difference in the original acids, which came from different bottles, and it would appear that the earlier distillation did not remove the last trace of impurities.

Results and Discussion

The isopiestic molalities of sodium chloride and of sulphuric acid solutions are given in Table I, together with the values of the activities of water in these solutions. The latter were obtained from the values of *R* listed by Janis and

TABLE I

ISOPIESTIC MOLALITIES AND THE ACTIVITY OF WATER IN SOLUTIONS OF SULPHURIC ACID AT 25° C.

m_1 Sulphuric acid		m_2 Sodium chloride		a_1 Activity	m_1 Sulphuric acid		m_2 Sodium chloride		a_1 Activity
4 349	4 351	(6 145)*		0 7530†	0 7338	0 7331	0 8174	0 8166	0 9729
4.348	4 347	6 142	(6 145)*	0 7531	0 6403	0 6398	0 7066	0 7065	0 9766
3.815	3 814	5 255	5 255	0 7936	0 5200	0 5193	0 5675	0 5675	0 9813
3.154	3 157	4 229	4 231	0 8404	0 3843	0 3841	0 4158	0 4162	0 9863
2 830	2 829	3 728	3 730	0 8628	0 2865	0 2868	0 3089	0 3089	0 9898
2 184	2 182	2 770	2 770	0 9023	0 1882	0 1880	0 2031	0 2032	0 9934
1.544	1 544	1 859	1 859	0 9367	0 0958	0 0957	0 1041	0 1042	0 9966
1 269	1 266	1 488	1 486	0 9500	0 04557	0 04545	0 0508	0 0511	0 99830
1.046	1 045	1 201	1 201	0 9598	0 01872	0 01880	0 02423		0 99918
0.8826	0 8814	0 9959	0 9959	0 9669					

* *Saturated solution.*

† *Gordon reports 0 7532 for a_1, based upon a new vapour pressure measurement by Shankman.*

Ferguson. For this purpose it is convenient to use a deviation curve based on the deviation of the values of the activity from those given by a linear function of the salt molality. This curve is itself linear in m_2 (NaCl) at the higher concentrations and therefore permits extrapolation to the saturated solution molality with a minimum of error. A plot of m_1/m_2 is shown in Fig. 1. The results of Scatchard, Hamer, and Wood are also included, the ratios having been calculated by us from their tabulated molalities. Several determinations that were too close together to plot separately are shown by a circle with lines indicating the number of measurements. Information concerning our duplicates is given in the table. For the saturated salt solution

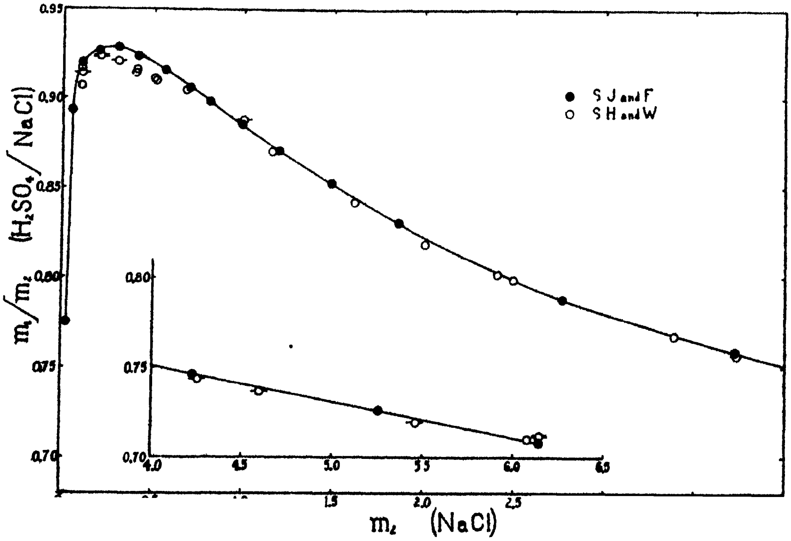

Fig. 1. The isopiestic molalities of solutions of sodium chloride and of sulphuric acid at 25° C.

their ratio is 0.7120, whereas our ratio is 0.7080, and the latter value agrees with their value at 6.0781 *m*. The molality of the saturated solution is given in I.C.T. (6) as 6.145; their isopiestic values range from 6.1429 to 6.1461, and our result is 6.142. The greatest discrepancy between the two series of results occurs below 0.5 *m*, and it was at this point that they altered their procedure. If the lowest point at 0.1 *m* is neglected, the difference here amounts to a vapour pressure difference of 0.0003 mm. of mercury.

A consideration of the Debye-Hückel and of the Duhem-Margules equations suggests that the ratio m_1/m_2 should approach the limiting value of 0.66 if the acid is a ternary electrolyte at great dilution. The high value that this ratio attains can mean only that the acid is essentially a binary electrolyte over most of the range investigated and becomes ternary only in dilute solution. Our curve indicates that but little of the second dissociation of sulphuric acid occurs above 0.2 *m* and that it increases rapidly below 0.1 *m*. This agrees with the experimental results and the conclusions of Dawson (1) in respect to this dissociation.

The activities of the water in sulphuric acid solutions at rounded molalities are given in Table II. The first column gives our values which were obtained from the experimental values by means of a sensitive deviation curve. The second column contains values calculated by us from the tabulated values of φ given by Scatchard, Hamer, and Wood. The latter values are not due to isopiestic measurements alone but represent their opinion of the best values indicated by the then available data. In Column III are given the rounded values of Gordon (3), which are based on the new vapour pressure measurements of Shankman. The details of this work will be published elsewhere in the near future. Harned and Hamer (4) calculated some of these activities from their e.m.f. measurements, and these are given in the fourth column.

The only serious differences occur at the higher molalities where our results agree with those of Gordon. The sodium chloride standard of Janis and Ferguson was originally confirmed in part by the use of potassium chloride

TABLE II

THE ACTIVITY OF WATER IN SOLUTIONS OF SULPHURIC ACID AT 25° C.

m_1 Sulphuric acid	a_1 S.J.F.	a_1 G.	a_1 S.H.W.	a_1 H.H.	m_1 Sulphuric acid	a_1 S.J.F.	a_1 G.	a_1 S.H.W.	a_1 H.H.
0.05	0.99814			0.99819	1.2	0.9530		0.9532	
0.1	0.99639		0.9964	0.9964	1.4	0.9440		0.9439	
0.2	0.9929		0.9928		1.5	0.9392			
0.3	0.9893		0.9892		1.6	0.9344		0.9341	
0.4	0.9858		0.9856		1.8	0.9240		0.9237	
0.5	0.9821		0.9819	0.9821	2.0	0.9128	0.9129	0.9129	0.9136
0.6	0.9783		0.9781		2.5	0.8837	0.8838	0.8837	
0.7	0.9743		0.9743		3.0	0.8513	0.8514	0.8514	0.8506
0.8	0.9703		0.9703		3.5	0.8164	0.8164	0.8161	
0.9	0.9662		0.9662		4.0	0.7797	0.7795	0.7781	
1.0	0.9620		0.9620	0.9620	5.0		0.7032		0.6980

solutions. It has now been confirmed over the whole range from 0.1 *m* to 6.0 *m* by the use of sulphuric acid solutions. Since the work of Gibson and Adams (2) was used to fix the standard at the high molalities, it is apparent that their measurements are in entire agreement with those of Shankman and Gordon.

The values for the activity of water in the acid solutions at molalities below 0.1 *m* were calculated on the assumption that the plot of a_1 against m_2 for sodium chloride was linear between $m_2 = 0$ and $m_2 = 0.1$. A similar assumption in respect to sulphuric acid would yield a value at 0.05 *m* of 0.99820, which agrees with the value of Harned and Hamer of 0.99819. If the first assumption is correct then these values would correspond to a ratio of m_1/m_2 of 0.93. That this must be incorrect is evident from an inspection of Fig. 1; the position of the ratio curve indicates the reason for our lower value of 0.99814.

Acknowledgment

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A NEW VACUUM ADIABATIC CALORIMETER[1]

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Abstract

A new adiabatic calorimeter is described in which transfer of the material under investigation from the thermostat to the calorimeter is effected through an evacuated space.

Introduction

In two earlier papers (1, 2) it was mentioned that a new adiabatic calorimeter was under consideration in the hope of continuing certain specific heat investigations with a higher degree of accuracy. The previous calorimeter (2, p. 212) had been developed to a stage where the accuracy of total heat measurements became dependent upon the technique of transferring the container and contents from the thermostat (at the desired initial temperature) to the calorimeter. As is usual in the case of many adiabatic calorimeters, this transfer was made through the air of the room, and the total heat measurements were thus subject to errors introduced by varying conditions of room temperature and humidity. Although attempts can be made to introduce corrections for these effects, such correction factors are always somewhat uncertain. It was deemed advisable, therefore, to eliminate the source of error by arranging for the transfer of the container through an evacuated space. It is with a description of this new vacuum adiabatic calorimeter that the present paper is concerned.

Description of the Calorimeter

A diagrammatic cross section of the calorimeter (not drawn to scale) is shown in Fig. 1.

The brass calorimeter jacket, *A*, is supported on metal legs inside a large galvanized iron vessel, *B*, of approximately 18 litres capacity. Filled with water, this vessel constitutes the adiabatic shield. The temperature is controlled by the addition of hot or cold water from jets of suitable sizes distributed conveniently around the rim of the vessel, *B*. Particular attention was paid to the stirring of this bath in order to avoid lag in the equalization of the temperature of the jacket wall. Efficient stirring is effected by four large double-bladed stirrers, alternate stirrers rotating in opposite directions.

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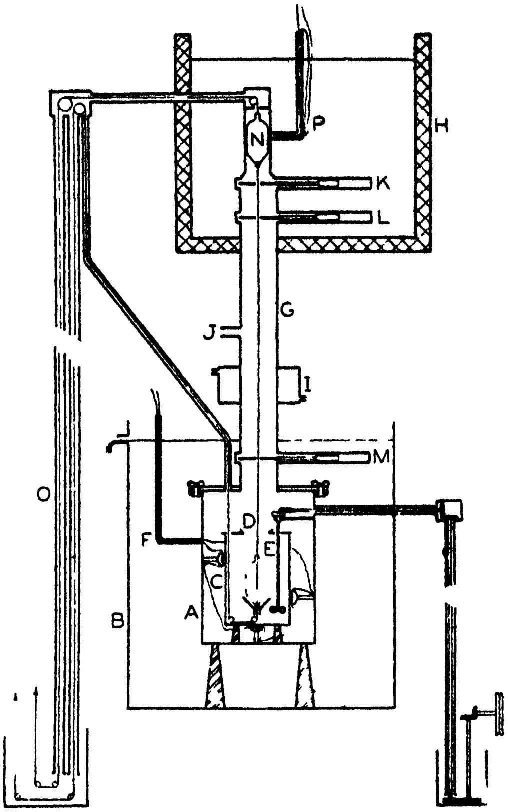

FIG. 1. *Vacuum adiabatic calorimeter.*

The calorimeter inner vessel, *C*, is of mild steel, highly polished, and has a capacity of about 500 cc. It is supported on three slender ebonite legs at a distance of 2 cm. from the bottom and walls of the calorimeter jacket. Since the calorimeter is operated with this space evacuated, the 2 cm. gap gives a sufficiently low thermal leakage modulus.

Owing to vacuum conditions, mercury is employed as the calorimetric liquid. The high density of mercury, of course, results in a much larger heat capacity for the calorimeter, and thus a smaller temperature change for a given quantity of heat introduced or removed than that for the same volume of water. Against this factor, however, may be set the advantage of eliminating the corrections necessitated by evaporation or condensation of the calorimetric liquid during temperature changes in the calorimeter (2, p. 208).

The thin cover, *D*, also of mild steel, is designed to permit free passage of the container, stirrer, and threads, and yet prevent loss of mercury due to splashing when the container is drawn rapidly into the inner calorimeter vessel.

The mercury in the inner vessel is stirred by means of a glass blade stirrer, *E*, with a very thin shaft; this reduces heat conduction to a minimum. The stirrer is rotated by a geared shaft passing out through the bath, *B*, so that its temperature always is the same as that of the calorimeter environment. Outside the bath, the drive is geared through a vertical shaft, 90 cm. long, which terminates in a reservoir of mercury. The casing of this shaft is vacuum tight, so that, when the calorimeter is evacuated, mercury rises in the casing to form an effective seal. The drive is operated by a controlled motor. The stirring of the calorimetric liquid is so regular and the time-temperature curves for each experiment are so smooth that it has not been necessary to employ synchronous stirring.

Between the calorimeter jacket and the inner vessel, nine pairs of copper-constantan thermels are arranged; eight in the form of a helix about the calorimeter vessel and one at the bottom. In this way, the temperature over the whole surface is integrated. The thermels are of the radiation type previously described (1). In the present calorimeter, the suspended junctions are at a distance of about 2 mm. from the wall of the inner calorimeter vessel. The thermel-galvanometer circuit is protected from the effects of stray electrical currents and unequal temperatures at the galvanometer binding posts in the same way as before (1, p. 72). The sensitivity of the present Leeds-Northrup D'Arsonval galvanometer is 11 mm. per microvolt at a distance of 1 m. The coil resistance is 18 ohms. With the present optical path of about 2.5 m., a deflection of 1 mm. on the mirror scale corresponds to a temperature difference of 0.00019° C. between the inner calorimeter vessel and the outer bath when the calorimeter is not evacuated, and to a difference of 0.00021° when the calorimeter is evacuated. The temperature of the outer bath can be maintained to within 0.0002° of that of the inner vessel for long periods of time without any difficulty.

The top of the calorimeter jacket, *A*, and its cover are flanged and held together by a number of wing nuts. An ungreased rubber gasket forms an effective seal. This gasket was cut to the exact shape of the flanged top of the jacket, and was rubbed into a wedge towards its inner circumference in order to relieve strain on the soldered joins between flange and jacket when the wing nuts are tightened.

From the cover, a brass tube, *G*, 3.5 cm. in diameter, leads into the thermostat, *H*, above the calorimeter proper. It is so constructed that when the container is drawn into the thermostat it makes good thermal contact with the walls of the tube, whereas it does not touch them during its passage to and from the calorimeter. A water cooler, *I*, is provided on the tube but was found to be unnecessary in the present work. The apparatus is evacuated at *J*.

To prevent radiation between the thermostat and the calorimeter proper, three steel shutters, *K*, *L*, *M*, are situated along the tube, *G*. The shutter, *M*, cuts out radiation into, or from, the inner calorimeter vessel by way of tube, *G*. The shutters *K* and *L* shield the container by isolating it when it is in position in the thermostat. A small piece of iron is attached to the handle of each shutter. A solenoid electromagnet (not shown in Fig. 1) is placed around the tube containing the arm of each shutter, so that by moving the magnet the shutter is drawn back and forth. A slit in each shutter permits passage of a thread, attached to the container, down the centre of the tube. The shutters are so arranged that, in the closed position, the slits are not parallel, and hence only a small opening down the centre, and occupied by the thread, remains. Tests made with the container in the thermostat and in the calorimeter and with the shutters open and closed have indicated conclusively that the shutters effectively cut out all radiation between the two sections of the apparatus.

The thermostat, *H*, consists of two concentric galvanized iron vessels. The outer one is approximately 2 in. greater in diameter and depth than the inner. The space between the two is filled with cork dust for thermal insulation. The thermostat has a capacity of about 12 litres. For initial temperatures above that of the room it is filled with glycoline and is heated electrically. The electric heaters consist of the element of an electric iron cut in half and soldered into thin copper envelopes. Such heaters are quite inexpensive to make and have proved to be remarkably free from lag. When the calorimeter is not in use, and also between runs, the thermostat is controlled by a large toluol thermoregulator working in conjunction with a sensitive relay. The toluol bulbs of the thermoregulator are fitted with copper gauze crosses throughout their length in order to ensure rapid attainment of equilibrium and consequently a minimizing of lag. The temperature of the thermostat is thus controlled to within ±0.02° C. For the half hour preceding the introduction of the container into the calorimeter, however, the thermostat is regulated by hand to within ±0.005° C. Efficient stirring is effected by means of a large triple-blade stirrer. The thermostat was tested with a movable set of thermels, and nowhere throughout the bath was a temperature gradient greater than 0.01° observed.

The platinum container, *N*, has a capacity of approximately 24 ml. It is "streamlined" to minimize splashing of mercury as it is drawn rapidly into the calorimeter, and to prevent mercury from being carried out of the calorimeter inner vessel as the container is returned to the thermostat. Transfer of the container is effected by means of a flax thread attached to either end of it and passing over the system of pulleys indicated in Fig. 1. The long columns, *O*, terminate in a mercury reservoir to provide a vacuum seal. From this reservoir the threads pass around a large, mounted wheel of approximately 32 in. diameter, to which they are fastened. A quarter revolution of this wheel effects the transfer of the container from the thermostat to the calorimeter. Its size is designed to afford complete control of the container during its rapid transit. A small weight is affixed to the wheel to hold the container beneath the surface of the mercury in the inner calorimeter vessel, *C*.

The thermocouple, *P*, was designed to indicate when the platinum container was in thermal equilibrium with the thermostat bath, and the approximate time required for equilibrium to be established. The inner junction was shielded to receive heat by radiation only from the container. The outer junction was in thermal contact with the oil bath near the thermometer bulb. The thermocouple was connected through clothes-pin switches to the same galvanometer as the lower set. This thermocouple, however, did not serve the whole purpose for which it was intended. At no time did it register zero deflection on the galvanometer while the thermostat was at an elevated temperature. The direction of the deflection seemed to indicate that the container was permanently at a lower temperature than the thermostat. The deflection was greater the higher the temperature of the thermostat, and when the thermostat was at room temperature, the deflection was zero. With an ice-water bath in the thermostat, a deflection in the opposite direction was observed. The deflection was small when the apparatus was under atmospheric pressure but was markedly increased on evacuation. Prolonged standing of the apparatus under reduced pressure did not cause the deflection to return to its original value; this indicates that the increased deflection was not a temporary effect set up on evacuation. Similar phenomena were observed when the container was not in the thermostat; this indicates that it was not the temperature of the container which the thermel was recording. Electrically insulated thermal contact between the inner junction and the container decreased the deflection markedly. The magnitude of the deflection indicated that a temperature difference of 0.1° C. existed between the two junctions of the thermel. It has been mentioned previously, however, that the temperature gradient throughout the thermostat was never greater than 0.01°.

This anomalous behaviour could be explained if the column *G* (Fig. 1) were conducting heat away from the inner junction rapidly enough to maintain the junction at a lower temperature than the thermostat. This did not seem probable, especially as an explanation of the increased deflection on evacuation. Furthermore, by placing first a steam jacket, and then an ice jacket, about the column where it emerges from the thermostat, no change in the galvanometer deflection was observed.

The more probable explanation is that the thermel leads themselves conduct heat away from the junction. This supposition receives support from a number of simple tests. For example, the two junctions of a copper-constantan thermocouple were sealed into identical thin glass tubes, the junctions themselves, being suspended in the centre of the tubes, while the double-silk-insulated leads from these junctions touched the walls throughout nearly all of their 10 in. length. The two tubes were placed side by side in a Dewar flask filled with finely crushed ice and distilled water. One tube was left at atmospheric pressure, the other was attached to a vacuum line. Originally the junctions registered zero deflection, but, when one tube was evacuated, a deflection was observed; this indicated that this junction was warmer than that in the unevacuated tube.

The tubes then were placed in a Dewar bath at 50° C. Again no deflection was observed with both junctions under atmospheric pressure, but, when one tube was evacuated, the observed deflection indicated that this junction was colder than that in the unevacuated side.

With both junctions in a thermostat at room temperature, only a temporary deflection, which returned to zero in a few minutes, was obtained.

The results of these tests can be explained satisfactorily only by conduction of heat along the thermel leads. In view of this fact, it was pointed out to workers with an electrical calorimeter in this laboratory that they might expect a similar effect along the leads used for their electrical input and voltage measurements of even greater magnitude, particularly at the temperatures produced by solid carbon dioxide in ether. They subsequently found it necessary to run their wires through a copper lead-in tube, immersed in the bath, many times the original length employed. In the case of the radiation thermels in the calorimeter proper, this difficulty does not arise since the lead-in wires and junctions are subject to the same environment.

In spite of its inability to indicate accurately any small temperature differences between the container and the thermostat, the thermocouple, *P*, did serve to show that temperature equilibrium is established between the container and the thermostat within 30 min.

Calibration of the Thermometers

The temperature of the outer bath of the calorimeter, and hence of the calorimetric liquid in the inner vessel, is determined by means of a platinum resistance thermometer, and a Mueller resistance bridge. The same galvanometer is used in this circuit as in that of the radiation thermels

The resistance thermometer was calibrated by measuring its resistance at 0° C. and at 100° C. in order to determine the fundamental interval. The value of the constant δ was supplied with the thermometer.

The determination of the ice point was made by immersion of the thermometer to a depth of nine inches in a Dewar flask filled with finely crushed ice and distilled water. Measurements were made with a current of 5 ma. through the thermometer. The ice point was reproducible to within $\pm 0.001°$.

A new hypsometer was designed for the determination of the steam point. Steam from a constant-level generator passed through a short length of exposed glass tubing and bubbled through a few centimetres of water in a Dewar flask to ensure saturation and to guard against superheating. The steam emerged from the Dewar flask through two insulated glass tubes that led to the hypsometer. The hypsometer consisted of two concentric glass tubes about 30 in. in length and having diameters of 2½ in. and 1½ in. respectively. The outside wall of the outer tube was insulated and the tops of both tubes were closed. The platinum thermometer was inserted to a depth of nine inches in the top of the inner tube. Steam entered both tubes at the top, so that the inner-tube was surrounded by a steam jacket and all air was expelled. Since both tubes were open at the bottom no pressure correction was necessary. Barometric readings were taken at the same times as the resistance measurements. The boiling points of water at the observed pressures were obtained from the International Critical Tables (5). This hypsometer proved to be very sensitive and, if desired, could be employed satisfactorily for the accurate measurement of changes in barometric pressure.

The values for the constants of the present resistance thermometer are as follows: R_0, 25.52974 ohms; F, 9.9486; δ, 1.5.

In order to facilitate the determination of temperatures, the resistance of the thermometer is calculated, with the usual Callendar formula, at one-half degree intervals over the temperature range in which it is to be employed, and direct interpolation is made in these intervals where, for practical purposes, a linear temperature-resistance relationship may be assumed.

With the present five-dial Mueller resistance bridge and galvanometer circuit, the resistance of the platinum thermometer can be estimated to within 5×10^{-5} ohms. This corresponds to a deflection of 1.5 mm. on the mirror scale.

Beckmann thermometers are employed to determine the temperature of the thermostat. They are standardized, as required, against the platinum resistance thermometer.

Manipulation of the Calorimeter

The container is drawn into its upper position in the thermostat and the three shutters *(K, L, M)* are closed. The temperature of the thermostat is regulated automatically to within ±0.02° of the desired initial temperature for at least one hour. Towards the end of this period, manual control of the thermostat to within ±0.005° is started, the calorimeter is evacuated, and stirring of the inner and outer calorimeter vessels is begun. Adiabatic conditions are established and then maintained by running hot or cold water as required into the outer calorimeter bath. The temperature of the bath is measured at five-minute intervals to determine the first portion of the time-temperature curve of the inner calorimeter vessel. After about 30 min., and at a recorded time, the three shutters are opened and the container is drawn down to its lower position in the calorimeter. The time of transfer is less than 1 sec. The weight is attached to the wheel in order to keep the container in position below the mercury level in the inner calorimeter vessel and the lower shutter, *M*, is closed.

Immediately before drawing the container into the calorimeter, a large hot water jet is opened to the outer calorimeter bath. As soon as the container is in position in the inner calorimeter vessel, the temperature of the outer bath is regulated so as to follow as closely as possible the rapidly changing temperature of the inner calorimeter vessel. Temperature equilibrium of the inner vessel is established in about 15 min., after which time the temperature of the outer bath again is recorded at five-minute intervals to determine the last portion of the time-temperature curve.

Finally, the shutter, *M*, is opened, the container is drawn back to its upper position, and the three shutters are closed. Air, carefully dried to eliminate effects of adsorbed moisture on subsequent evacuation, is admitted to the apparatus. The temperature of the outer calorimeter bath, *B*, is reduced to about 10° below the starting temperature desired (so estimated that the final temperature of the inner calorimeter vessel after coming to temperature equilibrium with the container in the next experiment shall be approximately 25° C.). In an hour the calorimeter is ready for another determination. Thus, once assembled, a large number of runs may be made under the same conditions without opening the apparatus at any point.

The Water Equivalent of the Calorimeter

Since the specific heats of certain of the materials of which the calorimeter is constructed (*e.g.*, glass and steel) are not known to a sufficient degree of accuracy, the water equivalent of the calorimeter was determined directly from a series of measurements with freshly boiled, distilled water in the container. At the same time, the opportunity was taken of studying the effect of the vacuum and of different times of transfer of the container. The results also indicate the degree of precision attainable with the apparatus in its present form.

The following sample data and calculations are typical of those involved in these determinations.

Wt. container, water, cement	= 74.6000 gm.
Wt. empty container	= 54.2875 gm.
Wt. water, cement	= 20.3125 gm.
Wt. cement	= 0.0051 gm.
Wt. water	= 20.3074 gm.
In vacuo correction	= 0.0215 gm.
Wt. water	= 20.3289 gm.
Initial temperature (thermostat)	
Beckmann thermometer	3.950°
Stem correction	0.031°
	3.981°
From standardization, this corresponds to	89.998° C.

Time-temperature Readings of Inner Calorimeter

Time, min.	0	5	10	10¼*	30	35	40	45
Resistance, ohms	27.44095	27.44115	27.44135		28.07005	28.07045	28.07075	28.07105

* *Container introduced.*

From Time-temperature Curve (2, p. 206)

Resistance at time container introduced	= 27.44136 ohms
Extrapolation of last portion of curve back to time container introduced gives	28.06896 ohms
Increase in resistance	= 0.62760 ohms
This corresponds to a temperature rise of	6.2487° C.
Final temperature of inner calorimeter (corresponding to 28.06896 ohms)	= 25.211° C.

The temperature rise (6.2487° C.) in the calorimeter divided by the temperature drop (89.998 − 25.211 = 64.787° C.) of the container and contents and multiplied by 65 gives 6.2692° C. as the temperature rise in the calorimeter for a 65° drop in the temperature of the container and contents.

From the average specific heats of water (5, vol. 5, p. 232) and of platinum (6, vol. 2, p. 1246) between 90° and 25° C. and assuming a value of 0.4 cal. per gm. per deg. for the specific heat of de Khotinsky cement, the total heat given up to the calorimeter by the known weights of these materials is as follows: water, 1320.64 cal.; platinum container, 112.338 cal.; de Khotinsky cement, 0.133 cal.—a total of 1433.11 cal.

It will be observed that, by this method of calculation, the initial temperature and the final temperature automatically are corrected to 90.00° C. and 25.00° C., respectively. This involves the tacit assumption that the specific heats at these temperatures are essentially the same as those at the actual temperatures observed. The assumption is justified by the fact that in all determinations the real initial temperatures (*i.e.*, approximately 90°, 75°, 65°, 50° C., respectively) and the final temperature (approximately 25° C. in all cases) were much less than one degree from the corrected values.

Since a volume of 3.85 cc. of air was enclosed with the water in the container, it is of interest to examine the magnitude of the total heats due to the following: *(a)* heat capacity of the air, *(b)* heat capacity of uncondensed water vapour in the air space, *(c)* latent heat of condensation of vapour.

(a) Heat Capacity of Air

The volume of air at room temperature was 3.85 cc. Taking the density as 0.0012 and the specific heat as 0 2, the total heat given up to the calorimeter during the fall in temperature from 90° to 25° C. is 0.06 cal.

(b) Heat Capacity of Uncondensed Water Vapour

Taking the vapour tension of water at 25° C. as 23.76 mm. of mercury (5, vol. 3, p. 212), the weight of uncondensed water vapour in the air space at 25° C. is 0.00009 gm. Taking the average specific heat (C_p) of water vapour as 0.443 cal. per gm. per deg., the total heat given up to the calorimeter by the water vapour in the volume of 3.85 cc. during the fall in temperature from 90° to 25° C. is 0.0026 cal.

(c) Latent Heat of Condensation of Water Vapour

Taking the vapour tension of water at 90° C. as 525.75 (5, vol. 3, p. 212), the weight of water vapour in the 3.85 cc. air space at 90° C. is 0.00159 gm. Thus the weight of vapour that condenses during the fall in temperature from 90° to 25° C. is 0.0015 gm. Taking the average latent heat of evaporation as 563.55 cal. per gm. (5, vol. 3, p. 212), the total heat given up to the calorimeter owing to condensation of water vapour in the container during the fall in temperature from 90° to 25° C. is 0.85 cal.

Of these correction factors, *(a)* and *(b)* may be neglected in comparison with the total heat of the water, container, and cement (1433.11 cal.). Furthermore, these two factors have increasingly smaller values for lower initial temperatures. The total heat brought down from each initial temperature must include, however, that due the latent heat of condensing vapour, *i.e.*, factor 3.

Hence the total heats given up to the calorimeter by the known weights of materials during a 65° drop in temperature are: water, 1320.64 cal.; platinum, 112.338 cal.; cement, 0.133 cal.; condensing vapour, 0.850 cal.; —a total of 1433.96 cal.

Dividing this total heat by the temperature rise (6.2692° C.) in the calorimeter gives 228.74 calories* per degree for the heat capacity of the calorimeter.

The results are summarized in Table I. The first column gives the number of the data for purposes of later identification. The second shows the corrected initial temperature of the container and contents. The third gives the time in seconds taken for the transfer of the container and contents from the thermostat to the calorimeter. The fourth indicates whether the apparatus was evacuated or not. The fifth records the number of determinations at each initial temperature. The sixth shows the heat capacity of the calorimeter. In each case the heat measurements have been corrected to a final temperature of 25.00° C. for the calorimeter.

TABLE I

HEAT CAPACITY OF CALORIMETER DETERMINED WITH DIFFERENT INITIAL TEMPERATURES AND UNDER DIFFERENT CONDITIONS OF TRANSFER

Data No.	T, °C.	Time, sec	Evacuated (*V*) or not (*A*)	No. of runs	H. cal./deg.
1	90.00	1	*V*	19	228.74 ± 0.04
2	75.00	1	*V*	16	228.68 ± 0.05
3	60.00	1	*V*	12	228.63 ± 0.05
4	50.00	1	*V*	9	228.58 ± 0.03
5	90.00	3	*V*	7	228.75 ± 0.06
6	90.00	5 to 6	*V*	7	228.91 ± 0.15
7	90.00	1	*A*	7	229.24 ± 0.08
8	90.00	3	*A*	6	229.37 ± 0.25
9	75.00	1	*A*	8	228.96 ± 0.13
10	60.00	1	*A*	5	228.69 ± 0.11
11	50.00	1	*A*	2	228.62 ± 0.03

Discussion

An examination of Table I shows immediately that the most satisfactory results with the new calorimeter are obtained when it is evacuated and when transfer of the container from thermostat to calorimeter is effected rapidly. Thus, from data 1 and 5 an increase in the time of transfer from 1 to 3 sec.

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* *Throughout this paper, quantities of heat are given in terms of the normal calorie.*

when the apparatus is evacuated does not alter the mean value for the heat capacity of the calorimeter, although the mean deviation from the mean is somewhat greater. However, when the time of transfer is extended to 5 or 6 sec. (data 6) both the mean value and the mean deviation from the mean are increased appreciably. This indicates an uncertain heat loss from the container with increasing delay during transfer. In view of the good agreement between the values for 1 and 3 sec., it follows that negligible heat loss is experienced at the shortest time of transfer, namely, 1 sec. It may also be noted that these data are for an initial temperature of 90° C., when heat loss during transfer should be a maximum.

From data 1, 2, 3, 4, 7, 9, 10, 11 it may be seen that, from each initial temperature, the mean value for the heat capacity of the container, as well as the mean deviation from the mean, is greater when the calorimeter is not evacuated. The differences decrease with lower initial temperatures and practically disappear for an initial temperature of 50° C. The values confirm the appreciable heat loss during transfer in air found with the old calorimeter (2), and vindicate the purpose underlying the design of the new vacuum apparatus. A comparison of data 1 and 5 with 7 and 8 shows rather effectively the advantage of transfers in vacuum as contrasted with similar transfers in air even though the air be dry.

The only unsatisfactory feature of data 1, 2, 3, 4 is the increasing value of the measured heat capacity of the calorimeter with higher initial temperatures. This indicates a small heat loss, probably from radiation, during transit of the container. Providing, however, that the calorimeter is calibrated experimentally, as in the present instance, over the range in which the specific heats of some other substance are to be determined, any error from this source can be eliminated by using the same container and an appropriate weight of the other substance so that the total heat brought down by the container and contents shall be approximately the same as during the calibration.

From the mean deviation from the mean values for the heat capacity of the calorimeter determined with the apparatus evacuated and for a time of transfer of 1 sec., the new calorimeter apparently is capable of an accuracy of certainly better than 0.05%, and probably of about 0.03%.

In view of this precision it would be of interest to redetermine the variation in the specific heat of water with the new calorimeter. The weight of the empty container, however, is too small to give a large enough rise in the temperature of the calorimeter for sufficiently accurate measurement. A mass of about 500 gm. of platinum would be required.

The new calorimeter has been employed for the determination of the specific heats of deuterium oxide over the temperature range 25° to 90° C. This investigation will be the subject of a later paper.

Acknowledgments

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STUDIES OF CARBON BLACK

V. THE EFFECT OF GAS COMPOSITION ON THE PRODUCTION AND PROPERTIES OF CARBON OBTAINED BY NON-IMPINGEMENT (LAMPBLACK) METHODS[1]

By L. M. Pidgeon[2]

Abstract

Lampblack has been produced from ethylene, propane, methane, and various mixtures of these gases. Carbon liberated from the flame of burning olefines is similar to carbon black in its ability to reinforce rubber, while carbon from paraffins resembles lampblack and does not reinforce rubber. The production of a reinforcing pigment by non-impingement methods is associated with a gas having a negative heat of formation.

Introduction

When a hydrocarbon burns in an adequate supply of secondary air, a luminous flame is produced. The luminosity is due to the presence of particles of carbon, which, being heated to the temperature of the flame gases, radiate in the manner characteristic of incandescent solid bodies. These particles are of minute dimensions and in most cases suffer complete combustion before escaping from the hot zone of the flame. Under suitable conditions, however, notably when the parent gas is a higher hydrocarbon or has a negative heat of formation, some of this carbon may escape from the flame and may be collected by suitable means. Carbon so formed is known as lampblack.

If, on the other hand, the flame impinges upon a relatively cool surface, carbon may be deposited thereon in the form known as carbon black. In practice, the lower members of the paraffin series, such as methane and ethane, are generally employed for this purpose. In the subsequent discussion the terms "impingement" and "non-impingement" will be employed to designate products of the carbon black and the lampblack processes.

While both lampblack and carbon black consist of carbon in a fine state of subdivision, their physical properties are very different. They are readily distinguished by their behaviour when dispersed in vulcanized rubber. Carbon black materially increases ultimate tensile strength and abrasion resistance, and has thereby become the most important reinforcing agent available to rubber technology in all applications where its "colour" is not an objection. Lampblack, on the other hand, does not reinforce rubber and finds restricted uses as a pigment.

While it is generally accepted that the major difference between impingement and non-impingement blacks is one of particle size, it has not been established whether this difference is due to the method of production or to

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other factors. Perrot (2) has pointed out that lampblack is normally produced from a complex mixture of hydrocarbons in which the constituents possess large molecules. These would be expected to yield larger particles than methane and its neighbouring homologues which are normally employed in the carbon black process. Wiegand (7), on the other hand, differentiates between the two types solely by the method of production, stating that either carbon black or lampblack may be produced from the same gas by choice of suitable methods.

The present work bears directly on this problem. The production of carbon by non-impingement methods has been carried out using a number of simple hydrocarbons both saturated and unsaturated. It has been found that the nature of the gas controls to a very considerable extent the properties of the carbon produced by this method. In general, gases consisting of olefines which have low heats of formation and high heats of combustion yield lampblack which reinforces rubber in a mannner analogous to the action of carbon black. Paraffins, on the other hand, yield typical lampblack.

It is, therefore, concluded that the particle size of the carbon is related to the heat of formation of the parent gas, paraffins forming large particles, while olefines and acetylene form smaller particles.

A. Production of Lampblack

1. *Apparatus*

The experimental lampblack apparatus as shown in Fig. 1 consisted of a vertical tube in which the gas was burned in a restricted supply of secondary air. The products of combustion subsequently passed through a filter which removed the carbon escaping from the flame. The gas issued from a 28% chromium steel tube, which terminated in a ½ in. orifice at *C*. The flow of air and gas was metered and controlled with suitable flowmeters, valves, and gasmeters. In early experiments, difficulty was experienced in producing a smooth flow of secondary air around the flame, and some flickering resulted. This trouble was obviated by the interposition of a number of horizontal sheets of stainless steel gauze *D* in the path of the air. With this arrangement a stationary flame could be produced; this is the condition productive of maximum yield.

In later experiments the tube was externally heated, in two sections, the preheat chamber *B* and the combustion chamber *A*. The approximate temperature of the walls of the tube was measured by means of thermocouples which were peaned into small holes drilled in the tube at the centre of each section.

The products of combustion were drawn into the filter *E* by a suction pump. Additional air was drawn into the chamber at *F* in sufficient quantity to cool the hot gases. This expedient allowed the use of a linen filter *E* backed by a wire gauze. The accumulated carbon was brushed from the cloth at regular intervals.

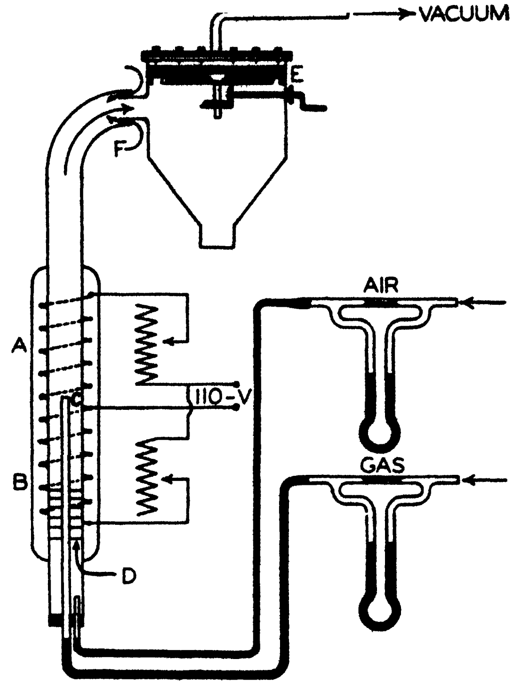

FIG. 1. *Apparatus.*

2. *Experiments in Unheated Tube*

In these experiments the air necessary to support combustion was drawn in by the natural draft of the vertical tube. The gas-air ratio was adjusted by altering the size of openings at the base of the tube. The optimum setting was obtained by trial, and remained constant throughout the experiments described in this section.

Tables I, II, and III show the yields of carbon obtained by partial combustion of various hydrocarbon gases. By varying the gas rate it was possible, with each gas, to pass through a point of maximum yield. The theoretical recovery was highest for ethylene and lowest for methane, as would be expected from a consideration of the heats of formation of these gases.

The same gases have been examined in an experimental carbon black apparatus (3, 4) and the following yields obtained:—methane-ethane, 1.3 lb.

TABLE I

PRODUCTION OF CARBON FROM ETHYLENE

Gas rate, cu. ft./min.	Yield, lb./1000 cu. ft.	% Theoretical recovery
0.062	3.3	5.3
0.051	4.4	7.0
0.033	3.7	5.9

TABLE II

PRODUCTION OF CARBON FROM 85 : 15
METHAN [illegible]

Gas rate, cu. ft./min.	Yield, lb./1000 cu. ft.	% Theoretical recovery
0 090	1.2	3.3
0.060	1.8	5.0
0.040	1.1	3 0

TABLE III

PRODUCTION OF CARBON FROM 70 : 30
PROPANE-BUTANE

Gas rate, cu. ft./min.	Yield, lb./1000 cu. ft.	% Theoretical recovery
0 075	4 0	3 9
0 060	3 7	3 6
0 043	5.1	4 9
0 031	6 2	6 0
0 027	7 0	6.8
0 013	6.6	6.4

per 1000 cu. ft.; propane-butane, 5 1 lb. per 1000 cu. ft.; ethylene, 4.3 lb. per 1000 cu. ft. If these results are compared with those appearing in Tables I, II, and III, it will be seen that this form of the lampblack apparatus is as efficient as the experimental channel carbon black apparatus.

3. *Experiments in Heated Tube*

Positive control of the gas-air ratio was possible in the apparatus as shown in Fig. 1. Under normal conditions a flame burning in secondary air in an enclosed space shows signs of stifling if the air supply is less than four times the theoretical requirements for complete combustion to carbon dioxide and water. In the present experiments it was possible to operate with less than the theoretical quantity of air, owing presumably to the fact that the flame temperature was maintained by the auxiliary heating of the tube.

(a) Ethylene—Results of experiments with pure ethylene are shown in Table IV. Optimum yields were obtained at low gas velocities and with an air-gas ratio about 60% of that required for complete combustion. As the air supply was decreased, the temperature in the combustion chamber decreased and more intense auxiliary heat was required to maintain the required temperature. The recovery of 13.3% of the carbon present in the gas is approximately double the maximum obtained in the unheated tube.

(b) Methane-ethane—Of all the gases under consideration, methane has the highest heat of formation and the lowest heat of combustion, and these properties are reflected in the heat requirements and carbon yields. As seen

TABLE IV

PRODUCTION OF CARBON FROM ETHYLENE

(Theoretical air-gas ratio for complete combustion is 15 : 1)

Gas, cu. ft./min.	Air, cu. ft./min.	Air : gas	T_A, °C.	T_B, °C.	Yield, lb./1000 cu. ft.	% Theoretical
0.03	0.25	8.3 : 1	1100	550	6 7	10.8
.03	.33	11.0 : 1	1100	550	7.0	11.2
.03	.40	13.3 : 1	1100	550	6 8	10.9
.02	.40	20 0 : 1	1000	550	7.5	12.0
.02	.30	15.0 : 1	1000	550	7.4	11.9
.02	.25	12 5 : 1	1000	550	8 3	13.3
.02	.18	9 0 : 1	1000	700	8.3	13 3
.02	.12	6.0 : 1	1000	700	7.3	11.7

in Table V the maximum yield was obtained with the theoretical air-gas ratio, any reduction in air supply resulting in lower yields.

With this gas the carbon recovery is 2.5 to 3 times that obtained by the channel process.

(c) Propane-butane—Results of experiments with this gas mixture are shown in Table VI. In this case, maximum recovery was obtained with less air than that required for complete combustion. Much less auxiliary heat was required than with methane, as would be expected from the higher heat of combustion of propane and butane. Yields were generally double those obtained in the unheated tube or in the channel apparatus.

(d) Synthetic mixture of ethylene (33%), methane-ethane (50%), and hydrogen (17%)—While pure ethylene is unlikely to be available in commercial quantities for the production of carbon black, mixtures of this gas with hydrogen and other paraffins are readily obtained by the pyrolysis of propane-butane, and similar gases. Experiments have already been described (4) in which gases produced in this manner have been utilized for the production of carbon black in an experimental plant of the channel type. It will be shown in the succeeding section that the lampblack produced from ethylene has

TABLE V

PRODUCTION OF CARBON FROM 85 : 15 METHANE-ETHANE

(Theoretical air-gas ratio for complete combustion approx. 10 : 1)

Gas, cu. ft./min.	Air, cu. ft./min.	Air : gas	T_A, °C.	T_B, °C.	Yield, lb./1000 cu. ft.	% Theoretical
0.02	0.20	10 : 1	1000	700	3.9	10.8
.02	.16	8 : 1	1000	700	2.5	6.9
.02	.12	6 : 1	1000	700	2.1	5.8

TABLE VI

PRODUCTION OF CARBON FROM 70 : 30 PROPANE-BUTANE

(Theoretical air-gas ratio for complete combustion is 25 : 1)

Gas, cu. ft./min.	Air, cu. ft./min.	Air : gas	T_A, °C.	T_B, °C.	Yield, lb./1000 cu. ft.	% Theoretical
0.02	0.50	25.0 : 1	1100	400	12.8	12.4
.02	.30	15.0 : 1	1000	550	13.0	12.6
.02	.15	7.5 : 1	1000	700	7.4	7.2

properties very similar to those of carbon black, and it therefore was interesting to ascertain the extent to which these properties would be maintained when an appreciable portion of the ethylene was replaced by other gases.

In Table VII the results of experiments on a synthetic gas are shown. In this gas an ethylene content of 33% replaces 25% ethylene, 3 to 4% propylene, and 1% acetylene contents, all of which occurred in these proportions in the pyrolysis off-gas referred to previously. The additional 8% ethylene was regarded as equivalent to the propylene-acetylene mixture in its ability to produce carbon. The carbon recovery based on the theoretical was 17% higher than any obtained previously.

TABLE VII

PRODUCTION OF CARBON FROM C_2H_4 33%, H_2 17%, CH_4 50%

Gas, cu. ft./min.	Air, cu. ft./min.	T_A, °C.	T_B, °C.	Yield, lb./1000 cu. ft.	% Theoretical
0.02	0.20	1000	700	5.6	15.6
.02	.20	1000	700	5.4	15.1
.02	.20	1000	700	5.4	15.1

B. Reinforcement of Rubber by Lampblack

While the physical properties of finely divided carbon may be evaluated in several ways, its behaviour in rubber has the greatest practical interest. Rubber tests have been carried out using the following formula: smoked sheet, 100; zinc oxide, 3; stearic acid, 2; sulphur, 5; diphenylguanidine, 0.75; carbon, 35 parts. Mixes were made on a laboratory roller mill and they were then vulcanized on a four-cavity mold in a steam press at 141.5° C. for various times as shown in the tables. Tensile tests were carried out with dumb-bell test pieces. Samples of standard channel blacks and lampblacks were examined simultaneously; hence curing and testing conditions were identical in any given group. Hardness was measured by means of the "Shore durometer".

Owing to the relatively low yields of carbon that are obtainable by means of all flame methods, it was not possible in every case to obtain sufficient carbon black to conduct full-scale rubber tests. The values appearing in Table VIII were obtained with a rubber mix of one-half the usual weight (281.5 gm.) employed in these experiments, and are in all cases lower than usual. The values in Table IX are more normal in this respect. Despite some discrepancies the results show clearly that the composition of the parent gas affects the physical properties of lampblack as exhibited in rubber.

TABLE VIII

TENSILE PROPERTIES OF RUBBER

Cure, min.	Modulus at elongation of					T_B	E_B	Hardness
	200%	300%	400%	500%	600%			
"F"								
65	34.0	62.0	106	146	217	227	620	55
85	43.5	85.0	131	189	256	256	600	55
105	43.8	86.0	131	185	245	249	600	58
"E" (produced from ethylene in unheated tube)								
65	55.6	88.5	138	220	262	262	600	60
85	52 3	74.6	132	206	270	270	600	60
105	40.5	77.0	130	192	252	272	620	57
Lampblack (Lumersheim)								
65	79.0	119.5	150	180	—	185	520	50
85	53.5	90.7	132	190	—	193	505	53
Cabot's "Spheron" (Channel black)								
65	40.0	63.5	125	184	—	242	560	53
85	39.0	76.5	128	186	248	264	630	55
105	45.0	86.0	144	206	—	267	600	53

In Fig. 2 the stress-strain curves at optimum cure are shown for carbons produced from various gases. The ethylene sample is almost identical with the channel black. The propane-butane sample, on the other hand, resembles a typical "soft" or "thermatomic" carbon producing a reasonably high ultimate tensile strength but exerting little stiffening. The commercial lampblack shows no reinforcement, so that the resultant product, while it is stiff, breaks short at low tensile values.

The carbons produced from olefines and paraffins in the heated tube showed less difference than those obtained in the unheated, but the superior reinforcement given by the carbon produced from the unsaturated gas was still very obvious.

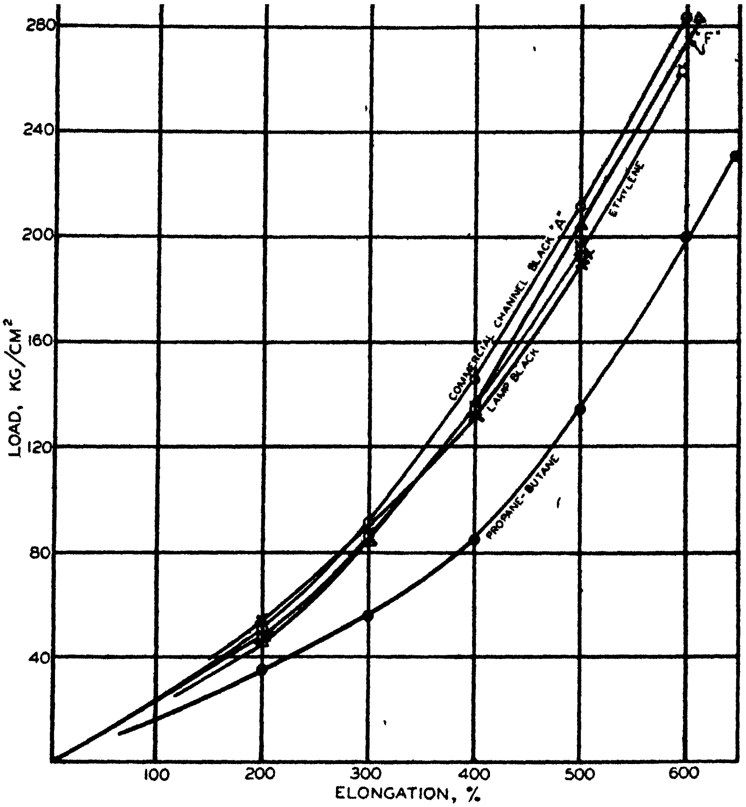

FIG. 2. *Reinforcement of rubber.*

Sample *F* was obtained from the upper portions and flues of the experimental channel carbon black apparatus described previously (4). When the apparatus was operated with gases rich in olefines the flames were very "smoky", and appreciable amounts of carbon escaped from the channels, a portion of which remained in the flues. It is generally considered that the carbon which escapes from the channels does not exhibit the properties of carbon black, and this is undoubtedly the case when the gas undergoing combustion consists of paraffins (5). When olefines are present, however, the properties of the resultant black resemble those of carbon black, as seen in Tables VIII, IX, and Fig. 2. In the case of a channel plant operating on olefine-bearing gases, it would be desirable to collect, if possible, the carbon escaping from the channels. If this procedure had been adopted in the experiments described previously (4), the yields obtained from pyrolysis waste gases would have been considerably improved.

The properties of carbon produced from synthetic gas of approximately the same content of olefines as the pyrolysis waste gases examined previously are only slightly inferior to those of carbon produced from pure ethylene, as shown in Table X.

TABLE IX

TENSILE PROPERTIES OF RUBBER

Cure, min.	Modulus at elongation of					T_B	E_B	Hardness
	200%	300%	400%	500%	600%			
N5 Propane-butane (Unheated tube)								
65	31.9	50.8	74.0	109	162	194	650	—
85	33.2	54.5	83.4	138	192	211	633	57
105	35.1	56.5	84.8	134	200	230	645	58
125	33.9	54.2	82.2	129	182	218	647	51
N13 Ethylene (Unheated tube)								
65	40.5	69.0	108	166	229	250	627	57
85	48.6	81.3	126	184	252	253	602	59
105	48.0	86.0	134	196	259	263	595	60
125	46.9	83.4	129	186	234	230	576	58
Cabot's "Spheron"								
65	37.3	66.3	108	169	227	267	653	57
85	41.5	77.1	124	193	264	289	630	58
105	50.8	92.5	146	212	284	284	595	60
125	54.4	94.8	153	215	287	284	596	63
'F'								
65	38.8	58.5	112	169	237	241	605	57
85	42.0	77.7	129	188	265	265	600	60
105	46.4	85.1	136	204	275	283	608	63
125	50.0	88.3	142	209	—	276	590	64

Conclusions

The reinforcement of rubber is probably a sorption process, this term being used in its widest possible sense. The magnitude of reinforcement will therefore depend on the bond existing between the carbon particle and the rubber molecule and on the size of the particle. Owing to the difficulty of measuring the former factor and to ignorance as to its real nature, it is convenient to consider that differences in reinforcement of rubber are due solely to difference in particle size, it being realized at the same time that this cannot be the only important factor. The particle size of lampblacks and thermatomic blacks is much larger than that of carbon blacks. This is indicated by oil adsorption, and by the opacity of dilute suspensions of known concentration. If, then, carbon black, which reinforces rubber, consists of fine particles, it may be concluded that the carbon which escapes from an ethylene flame has a much smaller particle size than that which escapes from a paraffin flame. This assumption seems to be readily reconcilable with the thermochemical properties of the gases.

TABLE X

Tensile properties of rubber

Cure, min.	Modulus at elongation of					T_B	E_B	Hardness
	200%	300%	400%	500%	600%			
Ethylene (Heated tube)								
65	26.6	51.0	80.0	125	182	235	670	50
85	33.6	57.5	90.3	141	210	260	660	54
105	34.7	59.0	88.0	140	210	262	660	52
125	33.6	60.0	91.8	148	209	246	660	53
Propane-butane (Heated tube)								
65	20.0	35.8	54.0	81.5	132	153	620	42
85	24.4	43.0	63.0	102	155	187	640	45
105	25.7	43.1	70.0	104	175	218	650	47
125	29.2	50.0	76.0	125	186	228	670	50
Ethylene, Methane, Hydrogen (Heated tube)								
65	24.4	43.0	71.5	111	176	212.2	650	47
85	30.0	53.5	85.0	142	205	254	660	48
105	35.8	62.5	97.0	161	225	247	610	51
125	35.8	63.5	97.5	160	232	252	620	53
Cabot's "Spheron"								
65	28.2	56.5	96.5	153	217	235	625	55
85	38.7	75.0	118	185	256	272	620	55
105	39.8	79.8	127	199	273	276	605	61
125	49.1	88.5	146	215	—	280	585	61

The dissociation of ethylene is exothermic to the extent of some 4000 cal. per mole. Ethylene dissociates readily in the gas phase since the required energy is already resident in the molecule and does not have to be supplied by radiation or conduction from hot zones outside the "cracking" region. Thus the reaction is largely homogeneous and a large number of small particles are formed which do not increase in size because, after their formation, the reaction is complete.

Paraffins, on the other hand, must be supplied with heat in order to cause dissociation, methane, the most stable paraffin, requiring some 21,000 cal. per mole. It is difficult to supply heat to gases as they are transparent to radiation and poor conductors of heat. Methane will not decompose in the gas phase at reasonable velocities until temperatures higher than 1200 ° C. are attained (6). At these temperatures the heterogeneous reaction is rapid. When a particle is formed by the dissociation of an activated hydrocarbon molecule it becomes a nucleus which is a good radiation absorber and will be maintained at a high temperature, thereby providing a surface upon which further heterogeneous reaction will take place. Thus as long as the particle remains in the heated zone it will grow in size.

In the channel process this agglomeration is arrested by the relatively cool plate, which collects a fraction of the particles before they have time to grow. In the lampblack process the particles have much longer time to aggregate, but, as we have seen, if the decomposition of the hydrocarbon is an exothermic reaction, the tendency is not greater than in the channel process.

If these conclusions are carried a step further, it seems clear that the addition of acetylene to paraffins would produce even finer particle sizes. It is possible that a suitable combination of acetylene and paraffin might produce by lampblack methods a carbon with properties identical with those of carbon black. The advantages of the process would be higher yields and the utilization of more compact apparatus. Large flames could be employed and the channel plant, with its enormous complication of piping and small burner tips and its high initial cost and corrosion problems, would be eliminated.

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SELENIUM IN CANADA[1]

BY HORACE G. BYERS[2] AND H. W. LAKIN[3]

Abstract

The existence of an enormous area of seleniferous soil is revealed through the results of a reconnaissance examination of portions of Alberta, Saskatchewan, and Manitoba provinces of Canada. About 300 samples of shales, soils, and plants were collected at 90 different locations. The selenium content of the shales varied from 0.3 to 3.0 p.p.m., and of the soils from 0.1 to 6 p.p.m. The vegetation contained from 3 to 4190 p.p.m. of selenium.

The investigations which have been carried out in the Department of Agriculture on the occurrence and distribution of selenium in soils have led far afield (3, 4, 5, 8), and have demonstrated, among other things, a close correlation between the geological strata from which soils have developed and the quantity of selenium found in the soils. Following up various indications, it has been shown that selenium in quantities sufficient to render some, though not all, forms of vegetation toxic is likely to be present in soils derived from Cretaceous shales. Areas of greater or less magnitude and of varied intensity of toxicity have been found in all the states where such soils occur, so far as they have been investigated. Among the areas examined one of the largest is the northern tier of counties of Montana (4, 8). The geological formations responsible for these soils include not only certain Cretaceous sediments but also pre- and post-Cretaceous formations (1, 2).

Geological formations of the same type cover enormous areas in the provinces of Alberta and Saskatchewan in Canada. At the suggestion of Dr. L. E. Kirk of Saskatchewan University, a reconnaissance examination of these areas was made in the spring of 1938. During a considerable portion of the examination the writers were accompanied by J. L. Bolton, of the Dominion Agricultural Experiment Station at Swift Current, who carried out the botanical identifications given in the text.

In the course of the investigations it has become very clear that certain plants may be used as "indicators" of seleniferous areas since they are certain to contain selenium if any is present in available form. Among these plants, known to occur under the soil and climatic conditions in west central Canada, are two species of *Astragalus* (*A. pectinatus* and *A. bisulcatus*). The examination of the area was therefore so timed that these plants would be in bloom and readily observed. In all, about 300 samples of shales, soils, and plants were collected at 90 different locations. These locations were selected, for the most part, because of the occurrence of the plants mentioned. In a few instances associated plants were included. The locations from which the

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samples were taken may readily be ascertained by means of automobile road maps of the area. No attempt will be made here to detail the data obtained. These data will be presented in a Department publication. The results may be summarized as follows:

The Geological maps of the Canadian Bureau of Mines, Nos. 204A and 267A, show extensive exposures of geological formations of the Cretaceous period which are identified under the names St. Mary's River, Fox Hills, Bearpaw, Belly River, Pakowki, and Milk River on the Calgary sheet (No 204A) in eastern Alberta and western Saskatchewan. These correspond in a general way with the Fox Hills, Bearpaw, Judith River, Claggett, Eagle, and Telegraph formations of Montana and to the various subdivisions of the Pierre formation in South Dakota and Nebraska (4, 6). No extensive outcrops of older Cretaceous formations corresponding to the Niobrara and other members of the Colorado shales are mapped.

Still larger areas of these shales are exposed formations shown on the Regina sheet (No. 267A) over the whole southern portion of Saskatchewan. Of these the most widespread are the Bearpaw and Belly River formations. Over considerable portions of both southern Alberta and Saskatchewan the actual soils rest upon post-Cretaceous formations which form irregular "islands" on the maps. Geological identification of the underlying strata in part of the area has not been published. A considerable portion of the area examined is covered by soils derived from Glacial Drift.

Of these shale formations about 50 samples were collected at 24 locations. All the samples on examination were found to contain selenium in quantities ranging from 0.3 to 3.0 p.p.m. In none of the concretions examined were there noted any showing concentration of selenium. In some instances astragalus plants were found growing in the shales. Notable among such cases is one at a point three miles north of Swift Current, Saskatchewan, where Bearpaw shale containing 1.5 p.p.m. of selenium supported an *Astragalus pectinatus* plant containing 3360 p.p.m. of selenium. Since vegetation containing more than 3 p.p.m. of selenium (7) may be regarded as somewhat injurious, this sample is to be regarded as intensely toxic.

Another sample of a fissile shale (presumably Judith River), 109 miles north of Swift Current on Route 4, contained 1 p.p.m. of selenium while the air-dry sample of *A. pectinatus* growing on this shale contained 2440 p.p.m. By contrast, a sample of shale 4½ miles northwest of Bow Island, Alberta (presumably Belly River formation), contained 0.5 p.p.m. of selenium, and *A. bisulcatus* growing in it had but 25 p.p.m.

Soil samples were taken at 80 locations. While usually these were only surface samples, in a few cases profiles were taken. All the soil samples were immediately under at least one of the plant specimens. The quantities of selenium found in the soil samples ranged from 0.1 to 6 p.p.m. and only at 25 locations did the concentration of the surface soil reach or exceed 1 p.p.m. The general character of the soils and the quantity of selenium found are similar to the conditions noted in northern Montana (8).

The purpose of the examination being simply a reconnaissance, no attempt was made to determine the degree of toxicity of food and forage plants. The indicator plants of the *Astragalus* family were used as a guide in selecting locations; and in general where neither *A. pectinatus* nor *A. bisulcatus* occurred, no samples were taken. Where these plants were found in abundance, occasionally other plants were selected, partly in the hope of finding other indicator plants. In all, about 100 plant samples were collected. The analyses of these plants are listed in Table I.

TABLE I

SELENIUM CONTENT OF ASTRAGALI SAMPLES FROM ALBERTA, SASKATCHEWAN, AND MANITOBA, CANADA

Lab. No.	Field No.	Location	Material	Selenium content, p.p.m.
Alberta				
B23069	17A	47 mi. W. of Maple Creek, 1 mi. W. of Pashley	*A. pectinatus*	640
B23070	18A	52 mi. W. of Maple Creek, 6 mi. W. of Pashley	*Poa secunda* (grass)	10
B23072	19A	5 mi. SW. of Medicine Hat, Route 3	*A. bisulcatus*	240
B23074	20A	16 mi. SW. of Medicine Hat, Route 3	*A. pectinatus*	3690
B23075	20B	16 mi. SW. of Medicine Hat, Route 3	Winter rye (immature heads)	8
B23077	21A	½ mi. E. of Bow Island, Route 3	*A. pectinatus*	3520
B23078	21B	½ mi. E. of Bow Island, Route 3	Young wheat (4 to 5 in.)	80
B23080	22XA	4½ mi. NW. of Bow Island on road to Ferry	*A. bisulcatus*	25
B23082	22YA	4½ mi. NW. of Bow Island on road to Ferry	*Dondia intermedia*	3
B23084	22ZA	4½ mi. NW. of Bow Island on road to Ferry	*A. bisulcatus*	30
B23086	23A	15 mi. W. of Bow Island on Route 3	*A. pectinatus*	370
B23088	24A	36 mi. W. of Bow, Route 3	*A. pectinatus*	1680
B23090	25A	1 mi. W. of Lethbridge	*A. bisulcatus*	470
B23098	26ZA	6 mi. NE. of Milk River	*A. pectinatus*	670
B23104	28A	12 mi. E. of Milk River (Verdigris Coulee)	*A. pectinatus*	340
B23118	30A	½ mi. N. of Coutts on Route 4	*A. pectinatus*	190
B23120	31A	4 mi. N. of Coutts on Route 4	*A. pectinatus*	280
B23122	32A	10 mi. N. of Coutts on Route 4	*A. pectinatus*	140
B23124	33A	32 mi. N. of Coutts on Route 4	*A. pectinatus*	150
B23126	34A	46 mi. NW. of Coutts on Route 4	*Thalaspi arvense* (stinkweed)	12
B23127	34B	46 mi. NW. of Coutts on Route 4	*Sisymbrium altissimum*	35
B23128	34C	46 mi. NW. of Coutts on Route 4	*A. pectinatus*	700
B23133	36A	93 mi. SE. of Calgary on Route 23	*A. pectinatus*	1260
B23135	37A	82 mi. SE. of Calgary on Route 23	*A. pectinatus*	460
B23140A	39A	1½ mi. E. of Morley	*A. succulentum*	25
B23146	42A	5 mi. W. of Calgary on Route 1	*A. pectinatus*	730
B23148	43A	20 mi. E. of Calgary on Route 9	*A. pectinatus*	1130
B23150	44A	20 mi. W. of Drumheller on Route 9	*A. bisulcatus*	60
B23152	45A	3 mi. N. of Drumheller on Route 9	*A bisulcatus*	140
B23155	46A	Lake Sullivan, 13 mi, SE. of Halkirk	*A. bisulcatus*	12
B23156	46B	Lake Sullivan, 13 mi. SE. of Halkirk	*A. goniatus*	25
B23157	46C	Lake Sullivan, 13 mi. SE. of Halkirk	*Homalobus tennellus* (Rydberg)	80
B23158	46D	Lake Sullivan, 13 mi. SE. of Halkirk	A. hay (mixed 46A, B, C) (3 years old)	20
B23160	47A	13 mi. SE. of Brooks on Route 2	*A. pectinatus*	1390
B23162	48A	36 mi. SE. of Brooks on Route 2	*A. pectinatus*	190
B23163	48B	36 mi. SE. of Brooks on Route 2	*Cheirinia inconspicua* (mustard)	10
B23164	48C	36 mi. SE. of Brooks on Route 2	*Pentstemon albidus*	60
B23166	49A	Medicine Hat on Route 2	*A. bisulcatus*	100
B23167	49B	Medicine Hat on Route 2	*Sideranthus grindelioides* (Rydberg)	10

TABLE I—*Continued*

SELENIUM CONTENT OF ASTRAGALI SAMPLES FROM ALBERTA, SASKATCHEWAN, AND MANITOBA, CANADA—*Continued*

Lab. No.	Field No.	Location	Material	Selenium content, p.p.m.
Alberta—conc.				
B23169	50A	5 mi. E. of Medicine Hat on Route 2	*A. pectinatus*	610
B23170	50B	5 mi. E. of Medicine Hat on Route 2	*Cheirinia aspera* (Prairie Rocket)	15
Saskatchewan				
B23025	5A	10 mi. S. of Outlook on Route 45	*A. pectinatus*	1000
B23027	6A	10 mi. W. of Elbow	*A. bisulcatus*	15
B23028	6B	10 mi. W. of Elbow	*A. missouriensis*	5
B23029	6C	10 mi. W. of Elbow	*Oxytropis gracilis*	4
B23030	6D	10 mi. W. of Elbow	*Chamaerhodos nuttalli*	20
B23031	6E	10 mi. W. of Elbow	*Astragalus* sp?	10
B23037	8A	4 mi. E. of Elbow	Yellow compositae	15
B23038	8B	4 mi. E. of Elbow	*A. pectinatus*	4060
B23039	8C	4 mi. E. of Elbow	*Aplopappus spinulosus*	260
B23041	9A	2 mi. S. of Herbert on Route 1	*A. pectinatus*	1150
B23044	11A	6 mi. W. of Cadillac	*A. bisulcatus*	1020
B23045	11B	6 mi. W. of Cadillac	*Hymenoxys Richardsonii* (Colorado rubber plant)	20
B23049	12A	4 mi. NE. of Eastend at exposure of Eastend formation.	*A. pectinatus*	1210
B23059	14A	9 mi. SW. of Eastend on Route 13	*A pectinatus*	160
B23064	15A	10 mi. S. of Maple Creek on Route 21	*A. bisulcatus*	50
B23065	15B	10 mi. S. of Maple Creek on Route 21	*Poa canbyi* (Scribn. Piper) "Canby bluegrass"	8
B23067	16A	12 mi. NW. of Maple Creek on Route 1	*A. pectinatus*	160
B23172	51A	13 mi. E. of Maple Creek on Route 1	*A. pectinatus*	2310
B23174	52A	60 mi. E. of Maple Creek on Route 1	*A. pectinatus*	790
B23015	1A	3 mi. N. of Swift Current on Route 4	*A. pectinatus*	3360
B23017	2A	24 mi. N. of Swift Current	*A. bisulcatus*	1150
B23176	53A	30 mi. N. of Swift Current on Route 4	*A. bisulcatus*	490
B23178	54A	35 mi. N. of Swift Current on Route 4	*A. bisulcatus*	340
B23180	56A	66 mi. N. of Swift Current on Route 4	*A. pectinatus*	120
B23180A	56C	66 mi. N. of Swift Current on Route 4	Large mushroom	10
B23019	3A	103 mi. N. of Swift Current on Route 4	*A. bisulcatus*	3640
B23021	4A	109 mi. N. of Swift Current on Route 4	*A. pectinatus*	2440
B23181	57A	7 mi. N. of Rosetown on Route 4	Young *A. bisulcatus* (on glacial drift)	3240
B23183	58A	3 mi. E. of Biggar on Route 14	*A. pectinatus*	220
B23185	59A	University campus, Saskatoon	*A. pectinatus*	1540
B23187	60A	13 mi. E. of Saskatoon on Route 14	*A. pectinatus*	780
B23188	60B	13 mi. E. of Saskatoon on Route 14	Young spring wheat	30
B23191	61A	64 mi. E. of Saskatoon on Route 14	*A. pectinatus*	1100
B23193	62A	164 mi. E. of Saskatoon on Route 14	*A. bisulcatus*	500
B23195	63A	3 mi. SE. of Kamsack on Route 8	*A. bisulcatus*	640
B23197	64A	3 mi. SE. of Kamsack on Route 8	Dandelions	110
B23200	65A	2½ mi. SE. of Kamsack on Route 8	*Hedysarum* sp?	60
B23202	66A	2½ mi. SE. of Kamsack	*A. bisulcatus*	350
B23208	68A	56 mi. SE. of Yorkton on Route 14	*A. bisulcatus*	320
B23223	77A	18.7 mi. N. of Burrows on road to Esterhazy	*A. bisulcatus*	420
B23226	79A	1 mi. W. of Broadview on Route 1	*A. pectinatus*	4190
B23227	79B	1 mi. W. of Broadview on Route 1	Western wheat grass	35
B23228	79C	1 mi. W. of Broadview on Route 1, 50 feet from 79.	*A. bisulcatus*	1020
B23276	80A	23 mi. W. of Grenfell on Route 1	*A. pectinatus*	1040
B23278	81A	61 mi. W. of Grenfell on Route 1	*A. pectinatus*	2590

TABLE I—*Concluded*

SELENIUM CONTENT OF ASTRAGALI SAMPLES FROM ALBERTA, SASKATCHEWAN, AND MANITOBA, CANADA—*Concluded*

Lab. No.	Field No.	Location	Material	Selenium content, p.p.m.
Saskatchewan—conc.				
B23280	82A	13 mi. S. of Regina on Route 6	Young wheat, 4 in.	120
B23282	83A	36 mi. SE. of Regina on Route 39	*A. bisulcatus*	1950
B23283	83B	36 mi. SE. of Regina on Route 39	Young wheat	140
B23285	84A	57 mi. SE. of Regina on Route 39	*A. pectinatus*	2370
B23287	85A	1 mi. SE. of Weyburn on bank of Souris River on Route 39	*A. bisulcatus*	2130
B23289	86A	22 mi. SE. of Weyburn on Route 39	*A. pectinatus*	650
B23291	87A	31 mi. SE. of Weyburn on Route 39	*A. bisulcatus*	830
B23292	87B	31 mi SE. of Weyburn on Route 39	Lambsquarters (*Chenopodium* sp?)	45
B23296	89A	13 mi. SE. of Estevan on Route 39	*A. pectinatus* (seeds)	2530
B23298	90A	24 mi. SE. of Estevan on Route 39	*A. pectinatus*	1050
Manitoba				
B23210	69A	½ mi. E. of Saskatoon-Manitoba line on Route 4	*A. bisulcatus*	330
B23213	71A	2 mi. E. of Saskatoon-Manitoba line on Route 4	*A. bisulcatus*	420
B23215	72A	17 mi. SE. of Russell on Route 4	*A. bisulcatus*	880
B23217	73A	5 mi. SW. of Mineota, base of bluffs of Assiniboine	*A. bisulcatus*	160
B23219	74A	4 mi. W. of Elkhorn on Route 1	*A bisulcatus*	890

Consideration of the data in Table I leads to a number of definite observations, especially when account is taken of previously obtained information and of the geological and geographical maps of the area.

Definitely, toxic vegetation is produced on soils derived from Cretaceous shales over very considerable areas in Alberta, larger areas in Saskatchewan, and a much smaller area in Manitoba. No estimate is offered concerning the number of square miles involved. Such estimate is not only impossible because of the limited scope of the investigation but because no attempt was made to sample areas not shown as Cretaceous, and when of Cretaceous origin, only if external indications of the presence of selenium were observed.

The samples of *A. pectinatus* (narrow leaf milk vetch) and of *A. bisulcatus* (two-grooved milk vetch) show the same variation of selenium content which has been observed elsewhere, and may be considered as indicating a wide variation in intensity of toxicity of the soils. In no case is selenium absent, the range being from 15 to 4190 p.p.m. None of the small number of other plants collected proves to be a selenium indicator except possibly *Homalobus tennellus*, 46C (*A. Tennellus* (Gray)), and *Chamaerhodos nuttalli*, 6D.

The samples of young wheat, 21B, 60B, 82A, and 83B, indicate the distinct possibility of toxic vegetation of the ordinary food or forage types. The sample 82A is especially interesting because it is from an area in which cursory investigation revealed no specimens of Astragali but the soil itself is very similar to seleniferous soils found in the United States. The quantities of selenium found in samples 15B, 18A, 20B, 34B, 48B, 48C, 64A, 79B, and 87B, also point clearly to the presence of moderately toxic areas of farm and ranch land and the probability of toxic food in certain areas.

One of the most interesting observations made was that in the section about Lake Sullivan, Alberta, hay, consisting in large part of *A. bisulcatus*, was used for feed during periods of feed shortage due to drought. One of these cases was investigated. The farmer in question reported that very little of this hay was actually eaten and that it was offered to the animals but once a week. His observation was that horses refused it absolutely and cattle and sheep ate it very sparingly. He considered this to be due to the presence of unpalatable fox tail which formed a large part of the hay. Since the animals refused the hay it was disposed of by use as thatch for the stables. The green plants in question and the three-year-old dry hay gave the results shown for numbers 46A, 46B, 46C, and 46D. It is clear that this material is unfit for forage and was so recognized by the animals themselves.

The data obtained point to the following:

While the existence of an enormous area of seleniferous soil is revealed and while definite evidence of injury is apparent, it does not follow that it presents a sufficiently serious situation to warrant any drastic remedial procedures except as further investigation of local areas may indicate. The evidence, taken together with previously assembled data, indicates very decidedly that overgrazing of the affected lands may produce serious injury through consumption by hungry animals of toxic plants not normally eaten by animals. It seems probable that within seriously toxic limited areas human injury may be produced when the total diet is composed of locally grown foods.

Supplementary observation and local information point to considerable injury to, and loss of stock through, troubles known locally as "frozen feet." One of the characteristics of selenium poisoning is malformation and even loss of hoofs of livestock, which effects can well be mistaken as due to freezing. How extensive this loss and how fully due to selenium poisoning may be ascertained only by detailed study of the areas.

The most important observation, aside from the extension of the area of seleniferous soils of toxic type, lies in the fact that glacial soils may be toxic. This fact points to a needed widening of the field of study in the United States.

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THE REACTION OF HYDROGEN AND DEUTERIUM ATOMS WITH PROPANE[1]

BY E. W. R. STEACIE[2] AND N. A. D. PARLEE[3]

Abstract

The reaction of hydrogen atoms with propane has been investigated over the temperature range 30° to 250° C. by the Wood-Bonhoeffer method. The products are solely methane at low temperatures, and methane, ethane, and ethylene at higher temperatures.

It is concluded that the results can be explained only by the assumption that the reaction

$$H + C_2H_5 \longrightarrow 2CH_3$$

is of importance. The bearing of this on the Rice-Herzfeld mechanisms is discussed. The activation energy of the reaction is 10 ± 2 Kcal.

The main steps in the postulated mechanism are:

Primary Reaction

$$H + C_3H_8 \longrightarrow C_3H_7 + H_2$$

Secondary Reactions at Low Temperatures

$$\begin{aligned} H + C_3H_7 &\longrightarrow CH_3 + C_2H_5 \\ H + C_2H_5 &\longrightarrow 2CH_3 \\ CH_3 + H &\longrightarrow CH_4 \end{aligned}$$

Additional Secondary Reactions at High Temperatures

$$\begin{aligned} C_3H_7 &\longrightarrow C_2H_4 + CH_3 \\ 2CH_3 &\longrightarrow C_2H_6 \\ H + C_2H_4 &\longrightarrow C_2H_5 \\ H + C_2H_5 &\longrightarrow C_2H_6 \\ H_2 + C_2H_5 &\longrightarrow C_2H_6 + H \end{aligned}$$

The reaction of deuterium atoms with propane was also investigated. It was found that the methane and ethane produced were highly deuterized, while the propane was not appreciably exchanged.

Introduction

The ethane decomposition has been extensively used as a proving ground for free radical theories [see (18) for references]. The original Rice-Herzfeld mechanism (11) for the ethane decomposition involved as the main steps the reactions:

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		E, Kcal.
(1)	$C_2H_6 = 2CH_3$	80
(2)	$CH_3 + C_2H_6 = CH_4 + C_2H_5$	20
(3)	$C_2H_5 = C_2H_4 + H$	49
(4)	$H + C_2H_6 = H_2 + C_2H_5$	17
(5)	$H + C_2H_5 = C_2H_4 + H_2$	Small
(6)	$H + C_2H_5 = C_2H_6$.	Small

This gives agreement with experiment in so far as the activation energy and the over-all order of the reaction are concerned. Various tests of the scheme have been made by investigating the part reactions. Patat and Sachsse (14, 15) used the ortho-para hydrogen conversion to measure the stationary hydrogen atom concentration in the system, and concluded that it was about 1000 times smaller than that predicted by the Rice-Herzfeld mechanism.

Investigations of the reactions of deuterium atoms with ethane by Steacie and Phillips (22) and by Trenner, Morikawa, and Taylor (28) lead to the conclusion that E_4 is about 8 to 9 Kcal. This removes the disagreement between Patat and Sachsse's results and the Rice-Herzfeld scheme in so far as the hydrogen atom concentration is concerned, but with the new value of E_4 the scheme no longer predicts a first order rate or the correct value of the activation energy of the over-all reaction (23).

In a recent paper Küchler and Theile (7) have shown that agreement with experiment can still be obtained, *i.e.*, a low H-atom concentration and the proper value of E_4 will still give the correct over-all E and the first order, if one assumes that the chain breaking process is not (6) but

(7) $$2C_2H_5 \longrightarrow C_4H_{10}\,,$$

and that the initial step is bimolecular, *i.e.*, in place of

(1) $$C_2H_6 \longrightarrow 2CH_3$$

we have

(1′) $$2C_2H_6 \longrightarrow C_2H_6 + 2CH_3\,.$$

It is thus still *possible* that the ethane decomposition proceeds by a free radical mechanism. Rice and Herzfeld (12) have critically examined and elaborated Küchler and Theile's mechanism. It should perhaps be emphasized that the exactness of the agreement of this scheme (or of any other) with experiment depends to a considerable extent on what value is taken as the over-all experimental activation energy. Estimates from various workers range from 69 to 77 Kcal. On account of difficulties connected with the back reaction and with side reactions, none of these estimates is very reliable, and the over-all activation is probably uncertain to 5 or 6 Kcal. This uncertainty makes it very difficult to make an unequivocal test of proposed mechanisms.

There is, however, a much more serious apparent discrepancy between the Rice theory and experiment which arises from the investigation of the reaction of hydrogen atoms with ethane. Trenner, Morikawa, and Taylor (28) found that methane was produced in this reaction, and concluded that the reaction

$$H + C_2H_6 = CH_4 + CH_3 \qquad (8)$$

had an activation energy several Kcal. lower than

$$H + C_2H_6 = C_2H_5 + H_2 . \qquad (4)$$

The production of methane in the reaction of hydrogen atoms with ethane was confirmed by Steacie (17).

Further information about the relative rates of Reactions (4) and (8) comes from the investigation of the mercury photosensitized reactions of ethane (19, 24, 25). Steacie and Phillips concluded that the mechanism of these reactions was:—

$$\begin{aligned} C_2H_6 + Hg(^3P_1) &= C_2H_5 + H + Hg(^1S_0) && (9)\\ H + C_2H_6 &= C_2H_5 + H_2 && (4)\\ H + C_2H_6 &= CH_4 + CH_3 && (8)\\ 2CH_3 &= C_2H_6 && (10)\\ CH_3 + C_2H_5 &= C_3H_8 && (11)\\ 2C_2H_5 &= C_4H_{10} && (7)\\ 2H &= H_2 && (12)\\ H_2 + Hg(^3P_1) &= 2H + Hg(^1S_0) . && (13) \end{aligned}$$

This mechanism accounts satisfactorily for the effect of various factors on the process and for the products of the reaction, hydrogen, methane, propane, and butane, provided that it is assumed that Reaction (8) is about four times as fast as (4). This assumption would make still more difficult the application of the Rice theory to the ethane decomposition, since it brings in Reaction (8) as a major step in the process. Actually, however, the occurrence of Reaction (8) would have much more serious consequences than this. All the Rice mechanisms are based on the idea that reactions of the type

$$R + HX = RH + X$$

occur readily, but that hydrocarbon chain splitting reactions of the type

$$R + CH_3(CH_2)_nCH_3 = RCH_3 + CH_3(CH_2)_n$$

never occur to an appreciable extent. Hence the ready occurrence of Reaction (8) is contrary to the general postulates of the Rice mechanisms for all substances.

In order to account for the production of methane, but at the same time avoid the postulation of chain splitting reactions like (8), Taylor has suggested (26) that methane formation occurs by

$$\begin{aligned} H + C_2H_5 &= 2CH_3 && (14)\\ H + CH_3 &= CH_4 . && (15) \end{aligned}$$

This mechanism has received theoretical support from papers by Rice and Teller (13), and Gorin, Kauzmann, Walter, and Eyring (4).

It is apparent from the above discussion that the decision as to the relative probabilities of Reactions (8) and (14) carries with it the fate of practically all the Rice mechanisms. Further information is therefore highly desirable, and, with this in view, experiments have been made on the reaction of hydrogen atoms with propane.

The only previous work reported on the reactions of H-atoms with propane was two runs made by Trenner, Morikawa, and Taylor (28) who reported that much more methane was formed than ethane, especially at low temperatures.

Experimental

The Reaction of Hydrogen Atoms with Propane

The reaction was investigated by the Wood-Bonhoeffer method, an electrical discharge being employed to produce atomic hydrogen. The apparatus was similar to that used in previous investigations (16).

Hydrogen was taken from a commercial cylinder, and passed through a quartz tube charged with platinized asbestos and heated electrically to 500° C. The gas then passed through a blow-off trap, through a liquid-air trap to remove water vapour and impurities, and finally gained access to the discharge through a calibrated capillary flowmeter.

Propane was obtained from the Ohio Chemical and Manufacturing Co. The gas contained less than 0.2% of impurities, and was used without further purification. Variations in the flow rate of both hydrogen and propane were accomplished by varying the pressure on the supply side of the capillary flowmeters.

The hydrogen was passed through a U-shaped Pyrex discharge tube of 2.5 cm. bore, about 1 metre long, to which were sealed side tubes containing cylindrical aluminium electrodes. The electrodes were attached to stout platinum wires, which passed out through the glass by means of capillary tubes and de Khotinsky seals. The discharge was operated with an applied voltage of 3500 across the tube and a 5000 ohm resistance. The current was maintained at 200 milliamperes by means of a rheostat in the primary of the transformer.

To obtain maximum efficiency the discharge was situated as close as possible to the reaction vessel. This was a Pyrex cylinder 7 cm. in diameter and 70 cm. long. It was surrounded by an electric furnace which could be slipped up and down the tube to permit observation when the efficiency of the wall poisoning, etc., was being tested. Two tubes entered the reaction vessel from below, one of which contained a thermocouple, while the other served as an inlet for the propane.

The walls of the apparatus were "poisoned" by means of phosphoric acid to prevent recombination of hydrogen atoms. The apparatus was first rinsed out with several litres of distilled water. This was followed by a cleansing rinse with fuming nitric acid, and a further washing with a large quantity of distilled water. The system was then washed out with a 5% solution of phosphoric acid, sealed up, and dried by evacuation through a liquid air trap. This treatment left a coating of metaphosphoric acid on the walls which under higher working temperatures probably dehydrated to phosphoric anhydride.

At any rate the poisoning insured a good working concentration of atoms for some months, providing that the temperatures used were not over 250° C. Above this temperature the anhydride slowly distilled to the colder parts of the apparatus, and the efficiency of the poisoning rapidly diminished.

The hydrogen atom concentration in the reaction vessel was measured by means of a Wrede gauge of the usual type (30). Atom concentration measurements could not, of course, be made by this method in the presence of propane Measurements were therefore made under nearly identical conditions of pressure, temperature, discharge current, and poisoning. The absence of the propane during these measurements made no great difference in pressure conditions, as the ratio H_2/C_3H_8 was high in most experiments.

The size of the reaction vessel and the speed of the pumps were such that the contact time was of the order of one second. After leaving the reaction vessel the products passed through a liquid air trap which removed propane and higher hydrocarbons, together with most of the ethylene and ethane. The remainder of the gas passed through a high-speed three-stage Leybold mercury diffusion pump. After leaving the diffusion pump the low boiling products were largely removed by a trap containing silica gel maintained at −180° C. The unadsorbed gas passed out through a Hyvac pump. The diameter of all tubing in the pumping and trapping system was about 2 cm., and all stopcocks were of correspondingly large bore.

At the end of a run, which normally lasted about two hours, the traps were allowed to warm up, and the products were pumped into a portable mercury gas holder by means of a Toepler pump. Trials showed that all the ethane and ethylene and virtually all the methane were trapped by the silica gel. A small amount of hydrogen was also retained by the gel.

The products of an average experiment amounted to 500 to 700 cc. Of this a 100 cc. sample was analysed by conventional methods in a Burrell gas analysis apparatus. This was done in order to keep a check on traces of CO, CO_2, and perhaps C_2H_2. The remainder of the products was analysed in a low-temperature distillation apparatus of the Podbielniak type. To prevent "freeze-ups" in the still, water and carbon dioxide were removed by dreierite and soda-lime before the distillation. In the distillation methane and hydrogen were taken off together, and this fraction was analysed by combustion.

Experimental Results

Sixteen runs were made at four different temperatures. The experimental results are given in Table I.

The results reveal two striking facts: *(a)* at low temperatures no ethane is produced, *(b)* no products heavier than propane are found. As these points are of great importance they were checked with considerable care. In the first place synthetic mixtures of H_2, CH_4, C_2H_6, and C_3H_8 were made up. Distillation analyses on these showed that it would not be possible to miss more than 0.5% ethane, and even this amount could usually be definitely

TABLE I

REACTION OF HYDROGEN ATOMS WITH PROPANE

Pressure = 0.36 mm.

Run No.	Temperature, °C.	Atom concentration, %	Propane flow, cc. per sec. at N.T.P.	Hydrogen flow, cc. per sec. at N.T.P.	Products of the reaction, mole per cent					Per cent of C_3H_8 reacted
					CH_4	C_2H_6	C_2H_4	CO_2	C_3H_8	
1	33	22	0.0690	0.517	23.2	0.0	0.0	1.0	75.8	9.60
2	31	22	0.0688	0.539	21.8	0.0	0.0	0.5	77.7	8.70
3	30	22	0.0674	0.521	18.0	0.0	0 7	0.3	81.0	7.55
4	32	22	0.0678	0.521	22.5	0.0	0.0	0.5	77.0	9.10
5	32	22	0 0603	0.515	19.2	0.0	0.0	0.5	80.3	7.60
6	30	22	0.0370	0.507	25.8	0.0	0.0	0.3	73.9	10.55
7	31	22	0.115	0.501	12.8	0.0	0 0	0.3	86.9	4.85
8	100	19	0.0687	0.526	13 5	3.2	0.8	0.5	82.0	8.35
9	100	19	0.0692	0.510	12 5	5.7	0.8	0.5	80 5	9.74
10	172	16	0.0705	0.526	9.7	11.7	1.4	0 6	76.6	13.69
11	171	16	0.0670	0.521	9.2	12 5	2.0	0 6	75.7	14.56
12	170	16	0.0698	0 526	8 8	10 1	1 5	0 6	79.0	12.10
13	170	16	0 0708	0.524	8 8	12.2	1 8	0.6	76.6	13 38
14	250	12	0.0693	0 505	—	—	3 3	0 7	—	—
15	250	12	0 0698	0 524	7 1	14.3	3.2	0 7	74 5	16.06
16	250	12	0.0700	0.524	5.7	14.0	3.2	0 6	76.3	15.09

detected. It may thus be stated with certainty that not more than 0.5% ethane was present in the products of the runs at low temperatures. The absence of hydrocarbons heavier than propane in quantities greater than 0.5% was proved by a few combustion analyses on the last portion of the distillate. A slight oiliness of the mercury in the Toepler pump was discerned after several runs, however, and this leads to the belief that traces of heavier products were present, probably hexane.

Table II gives the collision yield in the various experiments and the activation energies calculated on the assumption that the steric factor A in the equation

$$\text{Collision yield} = Ae^{-E/RT}$$

is equal to 0.1. In the table $Z_{C_3H_8,H}$ represents the number of collisions of one propane molecule with hydrogen atoms in the time considered. This is obtained from the relation (6, p. 46).

$$Z_{C_3H_8,H} = 2\sqrt{2\pi}\left(\frac{d_H + d_{C_3H_8}}{2}\right)^2 \sqrt{\frac{M_H + M_{C_3H_8}}{M_H\, M_{C_3H_8}} \cdot RT} \cdot N_H ,$$

where the d's are the molecular diameters, the M's the molecular weights, and N_H is the number of hydrogen atoms per cc. In making the calculation, $d_{C_3H_8}$ taken to be 4.2×10^{-8} cm. (27), and d_H to be 2.14×10^{-8} (2).

The Reaction of Deuterium Atoms with Propane

In the hope that some light might be shed on the nature of the secondary reactions, experiments were also made with deuterium atoms instead of hydrogen atoms.

The apparatus and technique were almost identical with those described in the previous section. The deuterium used was obtained from 99.6% deuterium oxide by treating it with calcium turnings. A slower flow rate was used with deuterium, so as to maintain approximately the same pressure in the apparatus as in the experiments with hydrogen. At the same pressure deuterium will flow through the apparatus more slowly than hydrogen and will thus take more time to get from the discharge to the reaction vessel. During this time, however, it will undergo fewer collisions on account of the lower molecular velocity. These two effects nearly balance and there will be no appreciable difference in the number of collisions undergone by hydrogen or deuterium atoms (or molecules) while travelling between the discharge tube and the reaction vessel. Also, the activation energies of the recombination reactions

$$\text{H} + \text{H}\,(+\text{M}) = \text{H}_2\,(+\text{M})$$

and

$$\text{D} + \text{D}\,(+\text{M}) = \text{D}_2\,(+\text{M})$$

will not differ appreciably. In view of these considerations there is no appreciable difference in the atom concentration in the two cases, and atom concentration determinations and other tests were made with ordinary hydrogen in order to conserve deuterium. In any case the possible error from this source is negligible compared with the uncertainties in the atom concentration due to fluctuations in the activity of the walls.

TABLE II

CALCULATION OF COLLISION YIELDS, ETC.

Run No.	Temperature, °C.	Total flow, cc. per sec. at experimental conditions (corrected for presence of atoms)	Reaction time, sec.	Partial pressure of hydrogen atoms, cm.	$Z_{\text{C}_3\text{H}_8,\text{H}}$ per sec.	$Z_{\text{C}_3\text{H}_8,\text{H}}$ in reaction time	Per cent reaction	Collision yield	E, Kcal. assuming $A = 0.1$
1	33	1540	0.890	0.0071	1.84×10^6	1.64×10^6	9.60	5.85×10^{-8}	8.7
2	31	1580	0.868	0.0071	1.85	1.61	8.70	5.40	8.7
3	30	1529	0.895	0.0071	1.85	1.66	7.55	4.55	8.7
4	32	1530	0.895	0.0071	1.85	1.66	9.10	5.50	8.7
5	32	1512	0.907	0.0072	1.87	1.70	7.60	4.45	8.8
6	30	1420	0.965	0.0074	1.92	1.85	10.55	5.70	8.6
7	31	1590	0.861	0.0066	1.72	1.48	4.85	3.30	9.0
8	100	1880	0.729	0.0061	1.44	1.05	8.35	7.95	10.4
9	100	1880	0.729	0.0059	1.39	1.01	9.74	9.65	10.2
10	172	2210	0.620	0.0051	1.10	6.82×10^5	13.69	2.00×10^{-7}	11.6
11	171	2170	0.631	0.0061	1.10	6.95	14.56	2.10	11.5
12	170	2180	0.628	0.0051	1.10	6.90	12.10	1.75	11.7
13	170	2180	0.628	0.0051	1.10	6.90	13.38	1.95	11.6
14	250	2450	0.559	0.0038	7.55×10^5	4.08	—	—	—
15	250	2540	0.540	0.0038	7.55	4.08	16.06	3.95	12.9
16	250	2540	0.540	0.0038	7.55	4.08	15.09	3.70	13.0

In the low temperature experiments, propane was collected in the liquid air trap, and combusted, and the resulting water analysed for deuterium. Methane together with some deuterium was adsorbed by the silica gel trap. Most of the deuterium was separated from the methane by passing the mixture through the distillation apparatus and drawing off the deuterium slowly, using maximum cooling. The remaining methane, containing a little deuterium, was combusted quantitatively and the water analysed for deuterium. The methane generally contained from 1 to 5% of deuterium, for which a correction was made in calculating the extent of deuterization of the methane. In making this correction, the deuterium was assumed to contain no light hydrogen. This assumption introduces no appreciable error, since with about 10% reaction with an 8 to 1 deuterium : propane mixture, the deuterium is over 90% heavy, and there is twice as much (hydrogen + deuterium) in a molecule of methane as in a molecule of "hydrogen", and only 1 to 5% of (hydrogen + deuterium) mixed with the methane. In the runs at higher temperatures where ethane and ethylene were also present, the products were trapped as before, and all pumped off together into a gas-holder. They were then separated by distillation, burned, and the resulting water analysed for deuterium.

Deuterium analyses were made in an apparatus of the Harteck type (5).

The results of the deuterium atom experiments are given in Table III. As methane and propane were the only products of the runs at 30° C., complete separation of the hydrocarbons was simple. The experiments at higher temperatures yielded considerable ethane which was highly deuterized. In Runs 5, 6, and 7 the uncertain end fractions were discarded and only the middle cuts were preserved for analysis. In the distillation apparatus used, the cut between methane and ethane was always quite sharp, but propane and ethane could not be separated so completely. In Runs 5, 6, and 7 the first 30 to 40 cc. of the propane fraction was discarded. The small percentage deuterization of propane in these runs pointed to two possibilities; either the

TABLE III

REACTION OF DEUTERIUM ATOMS WITH PROPANE

Pressure = 0 35 mm.

Run No.	Temperature, °C.	Atom concentration, %	Propane flow, cc. per sec. at N.T.P.	Deuterium flow, cc. per sec. at N.T.P.	Per cent deuterization of products			
					CH_4	C_2H_6	C_3H_8 uncorrected	C_3H_8 corrected
1	30	22	0 0690	0 370	—	Absent	<0 5	<0 5
2	30	22	0 0693	0 370	55 0	Absent	<0 5	<0 5
3	30	22	0 0698	0 370	62 3	Absent	<0 5	<0 5
4	30	22	0 0700	0 370	56 5	Absent	<0 5	<0 5
5	170	16	0 0692	0 370	High	52 8	3 4	<0 5
6	170	16	0 0708	0 370	High	65 8	2 5	<0 5
7	250	12	0 0700	0 370	High	54 0	2 2	<0 5
8	250	12	0 0692	0 370	High	—	<0.5	<0 5

propane was exchanged to the extent of about 2.5%, or it was undeuterized but contaminated with a small amount of deutero-ethane from the previous fraction.

To settle this point some highly deuterized ethane was prepared by thermally equilibriating ethylene and excess deuterium. This deutero-ethane was mixed with ordinary propane and distilled. An end fraction of 35 cc. containing ethane and propane was taken as in Runs 5, 6, and 7, and then three successive 35 cc. fractions of propane, *A*, *B*, and *C*. These samples were analysed for deuterium. In Run 8 a similar set of 35 cc. fractions was taken. The detailed results of these deuterium analyses appear below:

Run No.	Per cent deuterization				
	C_2H_6	$C_2H_6 + C_3H_8$ end fraction	Fractions of propane		
			A	*B*	*C*
Blank	49.0	25.0	7.8	<0.5	<0.5
Run 8	(57.5)	20.1	5.9	<0.5	<0.5

These results prove that the second fraction (*A*) was being contaminated by deutero-ethane, but that further fractions were uncontaminated. It may therefore be concluded that the real deuterization of the propane is less than 0.5%.

Owing to the small yield of methane at the higher temperatures it was found to be very difficult to separate enough of it to give a reliable analysis. Such determinations as were made indicated a high exchange.

Discussion

It is apparent from the above tables that the main facts in connection with the products of the reaction are:

(*a*) Methane is the only detectable product at room temperature.

(*b*) At 100° C. ethane is also formed in considerable quantity together with traces of ethylene.

(*c*) The amounts of ethane and ethylene increase with increasing temperature.

(*d*) Products heavier than propane are not present in detectable quantity.

In Fig. 1 the "collision yields" of the various products have been plotted against temperature. For the purposes of this plot the "collision yield" is defined as the number of molecules of a product formed per collision between a propane molecule and a hydrogen atom. By plotting the results in this manner, they are corrected for the variation in atom concentration with temperature, and for the variation in reaction time with temperature, pressure, etc.

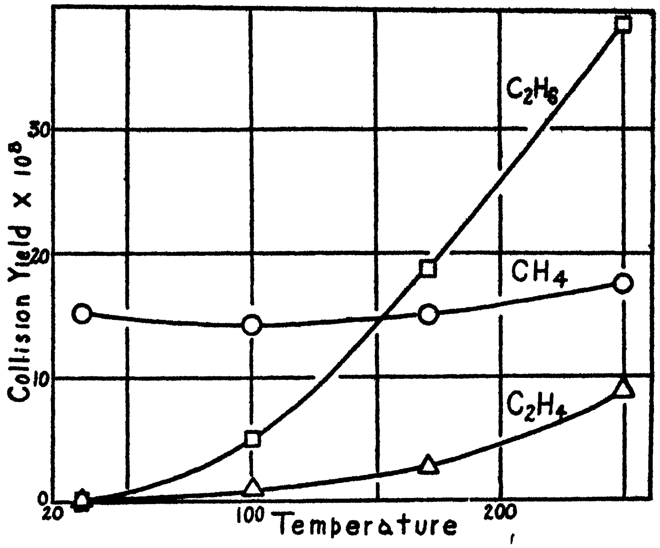

FIG. 1. *"Collision yields" of products in the reaction of hydrogen atoms with propane.*

Comparison of the results at room temperature and at 100° C. with the two runs recorded by Trenner, Morikawa, and Taylor shows good general agreement.

The Primary Reaction

There are obviously two possibilities for the primary reaction step, the abstraction of a hydrogen atom

$$H + C_3H_8 \longrightarrow C_3H_7 + H_2, \qquad (16)$$

or a hydrocarbon chain splitting reaction

$$H + C_3H_8 \longrightarrow C_2H_5 + CH_4 \qquad (17a)$$

$$H + C_3H_8 \longrightarrow C_2H_6 + CH_3. \qquad (17b)$$

Preliminary results on the mercury photosensitized reaction of hydrogen and propane by Steacie and Dewar (20) show that hydrogen and hexanes are the main products, the hexanes undoubtedly being caused by the recombination reaction

$$2C_3H_7 \longrightarrow C_6H_{14}. \qquad (18)$$

This suggests that (16) is the primary step, although the possibility of the occurrence of (17) in the present case cannot be ruled out on this evidence alone.

The non-appearance of hexane in our products is not surprising. In the mercury photosensitized reaction, the pressure is high and the hydrogen-atom concentration is very low. These conditions favour radical recombination reactions, and hexane is therefore to be expected if the propyl radical is present and has an appreciable life. Under the low pressures and high hydrogen concentration (atomic and molecular) of the Wood-Bonhoeffer method, collisions between propyl radicals will be relatively rare and the chance of a propyl radical reacting with hydrogen will be great. From these considerations the absence of hexane is to be expected, and cannot be offered as an argument against a primary step such as (16).

In general, it may be remarked that there is a very definite parallelism between the reactions of hydrogen atoms with ethane and with propane in so far as a comparison of the results of mercury photosensitization and of the Wood-Bonhoeffer method is concerned. In both cases large amounts of higher paraffins are obtained by mercury photosensitization (propane and butane from ethane, and hexanes from propane) while by the discharge-tube method only lower paraffins are obtained. The difference between the results of the two methods is, of course, due to the difference in the hydrogen-atom concentration and in the pressure.

Secondary Reactions at Low Temperatures

As stated above, the main feature of the results at 30° C. is the absence of ethane and ethylene in the products and the large production of methane. If the primary step were (17*b*) the results could not be explained on the assumption that the ethane formed disappeared by

$$H + C_2H_6 \longrightarrow CH_4 + CH_3 , \qquad (8)$$

since the apparent activation energy of this reaction is about 7 to 8 Kcal. (17, 28), and hence the reaction of hydrogen atoms with ethane at this temperature is not rapid enough to enable any ethane formed to be completely destroyed. Reaction (17*b*) may therefore be ruled out as a primary step. In any case (17*b*) is intrinsically less likely than (17*a*), since if a C–C bond is to be broken it is much more likely that the bond nearest to the approaching hydrogen atom will split.

If the primary reaction is (17*a*), then the ethyl radicals produced must react to form methane without the intermediate formation of ethane. The only way in which this can occur seems to be by the reaction

$$H + C_2H_5 \longrightarrow 2CH_3 , \qquad (14)$$

followed by

$$CH_3 + H \longrightarrow CH_4 . \qquad (15)$$

Taylor has suggested (26) that methane formation in the reaction of hydrogen atoms with ethane occurs by this means, as previously pointed out. The occurrence of reactions such as (14) is also supported on theoretical grounds by the recent work of Gorin, Kauzmann, Walter, and Eyring (4), and by Rice and Teller (13).

If the primary reaction is (16), then the propyl radicals produced must disappear without the formation of ethane. We cannot postulate appreciable decomposition of the propyl radical by the reaction

$$C_3H_7 \longrightarrow C_2H_4 + CH_3 , \qquad (19)$$

since all the evidence indicates that it is stable at room temperature (see Ref. 1). In any case the assumption of Reaction (19) would lead to new difficulties, since it has been shown (29) that the main product of the reaction of hydrogen atoms with ethylene is ethane, and neither ethylene nor ethane occurs as a product at low temperatures. It must therefore be concluded that if the primary reaction is (16) the propyl radicals produced disappear by a reaction analogous to (14), viz.,

$$H + C_3H_7 \longrightarrow CH_3 + C_2H_5. \tag{20}$$

If this is the case, then the ethyl radicals formed by (20) must disappear by (14).

It follows that, irrespective of whether the primary reaction is (16) or (17), the results at low temperatures can be accounted for only by the assumption that Reaction (14) occurs readily. The present results therefore furnish strong evidence for the occurrence of (14), and obviate the necessity of assuming reactions of the hydrocarbon chain splitting type like (8). The chain carrying steps in the Rice-Herzfeld mechanisms are therefore left at least qualitatively intact.

Secondary Reactions at Higher Temperatures

At higher temperatures methane production is diminished, and ethane and ethylene make their appearance. The production of ethylene is undoubtedly to be ascribed to the decomposition of the propyl radical at higher temperatures by Reaction (19). This is in agreement with the fact that the propyl radical can be detected in photodecompositions at ordinary temperatures by the Paneth technique (10), but cannot be detected in thermal decomposition reactions at higher temperatures (9). Bawn (1) estimates an activation energy for Reaction (19) of from 10 to 30 Kcal. The appearance of ethane at higher temperatures is also partly to be ascribed to the reaction

$$C_2H_5 + H_2 \longrightarrow C_2H_6 + H\,. \tag{21}$$

Leermakers (8) estimates an activation energy of 15 Kcal. or more for this reaction, but this estimate is perhaps somewhat high.

The presence of ethylene in the products indicates that the process

$$C_2H_4 + H \longrightarrow C_2H_5 \tag{22}$$

must be important as a source of ethane. The ethylene–hydrogen-atom reaction is known to be extremely fast even at room temperature (29), and only a greatly decreased atom concentration can account for the survival of an appreciable amount of ethylene in the products.

Examination of Fig. 1 and Table I shows that at 250° C. the production of ethane is roughly twice that of methane. Each propane molecule broken into must initially yield one mono-carbon and one di-carbon molecule. Hence, if no methyl radical recombination to form ethane occurred, the "collision yield" of methane would be expected to be equal to, or greater than, that of ethane plus ethylene. As this is not the case, ethane must be formed at high temperatures by methyl radical recombination. This will be favoured by high methyl and low hydrogen atom concentration, since the competing processes are

$$CH_3 + CH_3 \longrightarrow C_2H_6 \tag{10}$$

and

$$CH_3 + H \longrightarrow CH_4. \tag{15}$$

At high temperatures the presence of ethylene will lower the hydrogen-atom concentration by consuming hydrogen atoms, and Reaction (10) will therefore increase at the expense of (15). Taylor (26) has previously pointed out that the presence of ethylene serves to reduce the stationary hydrogen atom concentration to very small values.

The evidence that propane does not exchange with deuterium atoms under our experimental conditions makes it unnecessary to include any propane re-forming reactions in the mechanism.

The Activation Energy of the Primary Step

From Table II it will be seen that the apparent activation energy of the reaction as calculated from the collision yield rises from about 8.7 Kcal. at room temperature to 12 Kcal. at 250° C. This increase is probably not a real one, since the atom concentrations were determined with the Wrede gauge in blank runs, and the presence of ethylene undoubtedly lowers the stationary hydrogen-atom concentration in the runs at higher temperatures. Thus if it were assumed that the atom concentration at 250° C. was only 1% instead of 12%, E would be lowered from 13 Kcal. to 10.5 Kcal. In view of these uncertainties no very accurate estimate of the activation energy can be made. The most probable value would appear to be about 10 ± 2 Kcal.

Frankenburger and Zell (3) found large decomposition of pentane by hydrogen atoms, which apparently indicated increased reactivity with increasing molecular weight of the hydrocarbon. Our work, however, shows that propane is slightly less reactive to hydrogen atoms than is ethane. This is in agreement with preliminary experiments of Trenner, Morikawa, and Taylor.

There is, of course, the possibility of a propane re-forming reaction. Such reaction would have the effect of increasing the apparent activation energy of the primary step. This possibility was explored by the study of the propane-deuterium reaction, as discussed in the next section.

The Reaction of Deuterium Atoms with Propane

It will be seen from Table III that in the reaction of deuterium atoms with propane:

(a) The methane formed is highly deuterized,

(b) The ethane formed is highly deuterized,

(c) The unreacted propane is inappreciably exchanged, even at 250° C.

The methane deuterization is higher than can be accounted for by the mechanism previously discussed. This was also the case in the experiments of Trenner, Morikawa, and Taylor (28). It appears likely that the mechanism of this deuterization is that suggested by them, *viz.*, the formation and decomposition of a quasi-methane molecule.

$$CH_3 + D \longrightarrow CH_3D^* \longrightarrow CH_2D + H. \qquad (23)$$

This mechanism was also accepted by Steacie, Alexander, and Phillips (19) to account for the high deuterization of methane formed in the reaction of deuterium atoms with ethane.

The high deuterization of ethane may be partly due to the recombination of highly deuterized methyl radicals to form ethane. It is also probably due to the formation and decomposition of quasi-ethane as previously suggested by Steacie, Alexander, and Phillips,

$$C_2H_6 + D \longrightarrow C_2H_6D^* \longrightarrow C_2H_4D + H. \qquad (24)$$

The propane is inappreciably deuterized. This rules out the possibility of any propane re-forming reaction occurring to an appreciable extent. Reaction (20) must therefore be much faster than the recombination reaction,

$$H + C_3H_7 \longrightarrow C_3H_8, \qquad (25)$$

under our experimental conditions.

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A NEW TYPE OF SILICA TANNAGE[1]

By Alexander Rose[2]

Abstract

Silica tannage, usually in combination with other methods, has been extensively investigated, but no process in which silicon compounds were the principal agent has reached the commercial stage.

Ethyl and methyl orthosilicate have been found to possess a marked tanning action when hydrolysed in dehydrated or pretanned pelt. Details of the preparation of silica-tanned leather, analyses and hydrothermal behaviour of the resulting material, and significance of the new method of tannage are discussed.

Silica tannage, alone or in conjunction with every other possible tanning agent from alum to iron and from formaldehyde to zirconium, has been studied and discussed for more than a quarter of a century, but the investigations have usually been empirical in nature. In an early patent Morin (9) described a two-bath tannage, the prepared pelt being first immersed in a solution of an alkali silicate, then in dilute acetic acid, but the resulting leather was not satisfactory. Other investigators suggested the use of colloidal silicic acid or silicates as secondary tanning agents with marked filling properties. Bocciardo and Bocciardo (1) treated formaldehyde-tanned hide with silica sols prepared by neutralization of water glass solutions. Carpmael (2) and others used silicates as precipitants for salts of aluminium, cerium, iron, titanium, or zirconium in the treated pelt. Hough (4, 5) claimed to have developed a satisfactory method of tannage with stabilized silicic acid sols alone, but even in his more exhaustive studies such important data as shrinkage temperatures, resistance to hydrolysis, and aging characteristics have seldom been reported.

The present work, inspired by the more recent writings of Hough (5, 6) and the availability of pure ethyl orthosilicate (supplied by Carbide and Carbon Chemicals Corporation), was at the outset directed toward the development of a white leather that did not possess the shortcomings of the types now on the market, but the remarkable tanning action of the hydrolysis products of alkyl orthosilicates, $Si(OR)_4$, led to studies of a more fundamental character. The preparation, properties, and uses of the orthosilicic esters have received an increasing amount of attention during recent years, and will not be discussed in detail here. From the standpoint of this study the only important property of the lower alkyl orthosilicates is their susceptibility to hydrolysis, particularly by acid solutions.

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Preliminary Experimental Work

In the earlier experiments the unhaired and bated calfskin, washed free of borophenol preservative, was dehydrated in acetone, agitated in pure ethyl silicate for 24 to 72 hr., then transferred to the hydrolysing medium for a like period.

The first sample studied was shaken with ethyl silicate for 24 hr., then with distilled water for the same period, and tacked out while wet. The silica content (dry and oil-free basis) was 32.8%, and the shrinkage temperature was 77° C., as compared with 55 to 60° for the raw calfskin. Shrinkage temperatures were determined by fastening strips of the sample to the bulb of a thermometer and immersing in distilled water; the temperature was raised at a rate of about 5° per min., with constant stirring. The shrinkage temperature was taken as that at which the sample first showed appreciable curling, reduction in area, or, in some cases, the appearance of a distinct groove along the cut edge of the sample.

A second sample was shaken with ethyl silicate for 72 hr., hydrolysed in dilute acetic acid (pH = 3 0) for a further 24 hr., and tacked out while wet. The dried leather was highly plumped, resilient in feel, but rather cracky on the grain even after fat-liquoring. The silica content (dry basis) ranged from 47 to 54%, and the shrinkage temperature from 95 to 100° C., according to the point of sampling. The reduction in area when shrinkage took place was neither rapid nor extensive. Another sample, similarly treated with ethyl silicate, was hydrolysed in distilled water for 48 hr.; it had a silica content of 38 to 43%, and a shrinkage temperature (*Tg*) of 101 to 102° C. in glycerol solution; the grain was very cracky in this case, even after fat-liquoring.

Even more striking was the result when the dehydrated skin was immersed for three days in a mixture of 10% of 20° neat's-foot oil and 90% of ethyl silicate (by weight), and hydrolyzed in distilled water. The *Tg* was about 115° in a glycerol solution, but the sample was so stiff and cracky that this figure may be misleading; the silica content was 41.5% on the dry and oil-free basis.

In general, the highest loadings were obtained with samples of pelt from the looser and more open regions of the hide, and in many cases the silica content and shrinkage temperature were considerably lower than those indicated above, owing to poor penetration by the ethyl silicate. Later work was devoted to overcoming the crackiness of grain and non-uniformity of loading which led to the production of unsatisfactory leathers, all of which, however, were pure white when properly fat-liquored.

To overcome the crackiness of grain, as well as the wide variations in silica content which made systematic studies difficult, a number of expedients were tried: hydrolysis in fat-liquors, addition of neat's-foot and mineral oils to the ethyl silicate, vacuum impregnation of the dehydrated pelt after removal of the solvent, and vapour-phase hydrolysis of the silicate in atmospheres saturated with water vapour, sulphur dioxide, or both. The use of sulphur dioxide reduced the time required for hydrolysis from seven days to about three, for calfskin of normal thickness in saturated water vapour. The natural variations in the porosity of the pelt, together with the hardening or shrinkage of the raw pelt on dehydration with acetone (or, even more so, with methanol), militated against consistent results in this study. After a few experiments, an attempt to follow the progress of the diffusion of ethyl silicate into pelt dehydrated with acetone or methanol was abandoned, the results being highly erratic.

In the course of the work on vapour-phase hydrolysis, one very interesting observation was made. A piece of calfskin, dehydrated with methanol and shaken for three days with a mixture of 85% ethyl silicate, 10% neat's-foot oil and 5% white mineral oil (by weight), was tacked out, grain side up, in the laboratory for three days; the resulting leather was soft, full, resistant to tearing, and had a *Tg* of 98° C. with a silica content of 42.3% on the dry and oil-free basis.

In many experiments, including some in which vapour-phase hydrolysis was employed, the grain and flesh surfaces were heavily loaded and the centre of the pelt was obviously undertanned, with resultant low shrinkage temperatures. The more lightly tanned samples, however, were usually superior from the standpoint of resistance to tearing, suppleness, and strength of grain, all of which were low in the heavily loaded leathers, as might be expected.

A small quantity of methyl orthosilicate was synthesized and used in an attempt to increase the average loading and uniformity of results; its tanning properties on hydrolysis were found to be similar to those of the ethyl ester, but no great improvement in the rate of penetration or total loading was noted, despite the higher silicon content of the methyl ester.

Effect of Various Pretannages

The difficulties experienced in obtaining consistent results by the methods outlined above led to the use of various pretannages as a means of avoiding the inconvenience and detrimental effects (hardening, degreasing, etc.) of the dehydration stage and of keeping the hide in a soft and open condition for the subsequent silica tannage.

Alum tannage, or tawing, was found to be unsuitable; hydrolysis of the silicate in a fat-liquor, for example, removed most of the alumina and gave low fixation of silica and a poor leather, while vapour-phase hydrolysis of the silicate in the tawed pelt resulted in cracky grain and low shrinkage temperatures.

Certain studies by Meunier and Chambard (8) on neutralization of chrome leather with water glass solutions suggested that the colour of a chrome tannage could be masked by a sufficiently heavy loading with silica. The middle split of a commercial sample of chrome upper leather was degreased with acetone and impregnated with ethyl silicate; the original *Tg* of 90° C. was reduced to about 80°, probably because of the action of the fat-liquor used for the hydrolysis, and the colour was practically unchanged.

Finally, it was decided that formaldehyde pretannage was the only suitable method. The usual procedure was to drum the bated calfskin for 9 to 12 hr. in about five times its weight of saturated borax solution (pH = 9.1), then add 40% formalin solution in three or four portions over a period of three days until the total amount of formalin solution was 5% on the white weight. The tanned stock was washed thoroughly and tacked out to dry, then lightly fat-liquored and staked. The *Tg* was 84 to 86° C. as compared with 60 to 62° for the bated calfskin.

Impregnation with ethyl or methyl silicate and hydrolysis in a fat-liquor did not raise the *Tg* of the pretanned material unless the final silica content was 25 to 30% or higher; again, the results were erratic owing to lack of uniformity in the absorption of silicate by the pretanned material. The maximum increase in the *Tg* of any sample was about 10° C. Likewise it was found that formaldehyde solutions with pH values between 7 and 8 increased the *Tg* of silica-tanned leathers by 5 to 15° in certain cases. The sharp and extensive shrinkage characteristic of formaldehyde-tanned leather persisted after silica tannage.

Discussion

It would be unwise to indulge in extensive theoretical speculation on he basis of the somewhat scattered results summarized above. There can, however, be no doubt that hydrolysis products of ethyl and methyl silicate have, under appropriate conditions, a true tanning action, the mechanism of which is a matter for future elucidation. Under the conditions of hydrolysis employed in the present work the state of molecular aggregation and chemical reactivity of the silica formed, together with its proximity to the protein fibrils at the moment of formation, would lead to a type of combination markedly different from that obtained by tannage with so-called "colloidal silicic acid", prepared by neutralization and stabilization of solutions of alkali silicates, or by acidification of hides previously treated with water glass solutions.

Hurd (7) has pointed out in a recent review that hydrated silicic acid when first formed by acidification of alkali silicate solutions may have a molecular weight corresponding roughly to the monomeric condition, that in this state it may pass readily through the usual types of dialysing membranes; and condenses rapidly to complexes of very high molecular weight. If an active group in such a complex should react with active groups in the protein chains, the marked tanning action of the freshly formed silica would not be surprising. Hough (5) has stated that silica tannage may be conveniently combined with formaldehyde tannage but does not improve vegetable-tanned leather; he suggested that the vegetable tannins and silicic acid probably combined with the same groups in the collagen structure. The small increase in shrinkage temperature when formaldehyde-tanned leather is given a subsequent silica tannage points to a similar explanation, since it is generally agreed that formaldehyde tannage takes place at the amino and imino groups. If the silica does combine with these basic groups, then the pH of the hydrolysing medium would probably affect the rate and effectiveness of the tannage, as well as the rate of hydrolysis of the orthosilicate ester. On the other hand, the tanning properties may be due to purely physical protection of the protein chains by strongly adsorbed layers of silicic acid micelles.

While the tannage described is hardly of commercial importance under present conditions, the tanning properties of the hydrolysis products of the alkyl orthosilicates deserve further study. The difficulties described in the present paper might be overcome to a certain extent by the use of carefully graded hide powder as raw material. Quantitative hydrolysis studies by the method of Gerngross and Gorges (3) on hide powder tanned with silica, formaldehyde-silica, or chrome-silica; X-ray spectrographic studies; investigation of the effects of various conditions (pH, temperature, etc.) during hydrolysis of the silicate; tannage with silica produced by hydrolysis externally as well as *in situ;* studies of the rate of hydrolysis of the orthosilicic esters and the state of aggregation of the resulting products;—these and other experimental approaches suggest themselves. The results may throw some light on the mechanism of tanning in general, and of formaldehyde and vegetable tanning in particular, which will justify the effort involved.

Acknowledgment

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STUDIES IN ISOUREAS AND ISOUREIDES

V. THE ADDITION OF DIHYDRIC AND SUBSTITUTED ALCOHOLS TO CYANAMIDE[1]

By S. Basterfield[2], F. B. S. Rodman,[3] and J. W. Tomecko[4]

Abstract

In continuation of earlier studies on the formation of alkyl-isoureas by the addition of alcohols to cyanamide, a series of new isoureas has been prepared from ethylene glycol, glycol mono-ethyl ether, glycol mono-acetate, ethyl glycollate, ethanolamine, and resorcinol. In addition, the preparation of allyl-isourea, which had previously failed, *m*-nitrobenzyl- and cyclohexyl-isoureas was accomplished. The new isoureas were characterized by the preparation of salts (salicylates or benzoates), and of cyclic isoureides by condensation with acetoacetic and malonic esters. Some further study was made of benzyl- and phenylethyl-isoureas, previously prepared in this laboratory.

In an earlier study (2), it was shown that the formation of isoureas, by the addition of anhydrous alcohols to cyanamide in the presence of hydrogen chloride, generally takes place readily at room temperature. The rate of addition was found to vary considerably with the nature of the alcohol, the time of disappearance of the reaction for free cyanamide ranging from 24 hr. for methyl and ethyl alcohols, to seven to eight days for benzyl and phenylethyl alcohols. Unexpectedly, allyl alcohol appeared to react very slowly, and from the dark-coloured residue obtained after long standing, no isourea was isolated. In the present study, carefully purified allyl alcohol was found to react quite smoothly with cyanamide, with the production of allyl-isourea in good yield. It is apparent that some unknown impurity was responsible for inhibiting the addition reaction in the earlier investigation.

In the present investigation a new series of isoureas has been prepared by the addition to cyanamide of the following alcohols: ethylene glycol, glycol mono-ethyl ether, glycol mono-acetate, ethyl glycollate, ethanolamine, and *m*-nitrobenzyl alcohol. In addition the preparation of cyclohexyl-isourea (previously recorded (1)) is described and further study of benzyl- and phenylethyl-isoureas reported.

The experiments reported in this paper show that while ethylene glycol reacts with cyanamide with a speed comparable to that of the simple monohydric alcohols, the glycol ether and acetate are far less reactive, and seem to fall into a group with ethyl glycollate and resorcinol. Ethanolamine is remarkable for its extraordinarily low speed of reaction. It is an exceptional case in that two equivalents of hydrogen chloride are required for the reaction, the basic group of the alcohol absorbing one equivalent. Although β-β′-dihydroxy-ethyl ether appeared to react almost as fast as the simple alcohols, no isourea was obtained from the reaction. The reaction has not been examined further.

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TABLE I

ADDITION OF ALCOHOLS TO CYANAMIDE

Alcohol	Time of disappearance of cyanamide		Molar ratio alcohol/cyanamide	Solvent
	20–22° C.	40° C.		
Methyl	24 hr.	18 hr.	12 : 1	Reacting alcohol
Ethyl	26 hr.	23 hr.	12 : 1	Reacting alcohol
Allyl	5 days	22 hr.	12 : 1	Reacting alcohol
Cyclohexyl	24 hr.	—	12 : 1	Reacting alcohol
Glycol mono-ethyl ether	18 days	5 days	12 : 1	Reacting alcohol
Ethylene glycol	41 hr.	18 hr.	1 : 1	Ethylene chlorhydrin
Glycol mono-acetate	36 days	5 days (+)	1 : 1	Ethylene chlorhydrin
Ethyl glycollate	20 days	5 days	1 : 1	Ethylene chlorhydrin
Resorcinol	23 days	5 days (−)	1 : 1	Ethylene chlorhydrin
Ethanolamine	12 months	7 months	1 : 1	Ethylene chlorhydrin

The rates at 40° C. are more significant for comparison since, at room temperature, a precipitate of cyanamide dihydrochloride was often formed when hydrogen chloride was added, and the amount of the former varied with different alcohols as did also the rate at which it disappeared. An excess of hydrogen chloride above the required equivalent definitely reduced the rate of addition. In one preparation of ethyl-isourea, two equivalents of hydrogen chloride were added in error, and the reaction for cyanamide disappeared only after a week had elapsed. The effect of excess hydrogen chloride was confirmed by other experiments. On the assumption that free alcohol is the reactant, this effect may be due to the combination of alcohol with hydrogen chloride to form the oxonium salt, which decreases the concentration of free alcohol. This may be true despite the fact that the reaction does not proceed at all in the absence of hydrogen halide. The influence of increased concentration of alcohol was readily apparent when larger molar ratios of alcohol to cyanamide than 12 : 1 were used. With methyl and ethyl alcohols, the excess of which could be readily removed, the reaction time was reduced to about 12 hr. at room temperature, and with very pure cyclohexanol to about 14 hr.

It is interesting to observe that both ethylene glycol and resorcinol yielded only mono-isoureas; in other words, only one hydroxyl group functioned.

If di-isoureas were formed they were not present in sufficient quantity to be isolated.

Benzyl- and phenylethyl-isoureas were prepared in the previous study (2), but because of the smallness of the yields and the fact that only the salicylates were analyzed, it was thought desirable to repeat the work and characterize these isoureas further by means of condensation products. The salicylate of phenylethyl-isourea was found to melt at 158° C. as compared with 134° C. recorded by Basterfield and Powell (2). The analysis for nitrogen also gave figures closer to the calculated result than did the analysis of the earlier product. (Calcd.: N, 9.27%. Found: N, 9.33, 9.24%. Previous analysis:—found: 8.94, 8.94%). Samples of both the older and newer preparations were examined microscopically. The older material contained amorphous masses and the crystals were poorly defined. The newer material consisted of well defined rectangular crystals and was free from amorphous particles. The older material was carefully recrystallized from alcohol until it was free of amorphous material, and the crystals were of good form. The melting point was then found to be 158° C.,[†] identical with that of the newer preparation.

In the preparation of the isourea hydrochloride the general method was modified to suit the type of alcohol employed. When the alcohol was sufficiently volatile to be distilled under reduced pressure at a moderately low temperature, it was used as the medium for the reaction, and the excess was removed by distillation when the addition reaction was complete. For less volatile alcohols, equimolecular proportions of alcohol and cyanamide were dissolved in ethylene chlorhydrin (10 to 12 moles) which does not react with cyanamide. The isourea hydrochloride was precipitated by pouring the reaction residue into ice cold ether, after most of the solvent had been removed by distillation at low pressure.

The free bases were liberated from the crude hydrochlorides, which were oils or semicrystalline masses, by treatment with powdered sodium or potassium hydroxide in contact with moist ether. Since some of the bases were unstable and their ether solutions became turbid from the separation of polymerized decomposition products, the ether solutions were filtered rapidly into an ether solution of salicylic or benzoic acid. The salicylates or benzoates usually separated rapidly. They were filtered off and recrystallized from alcohol. The more stable bases were obtained from the ether solutions as oils or low melting point solids and mixed with the required amount of acetoacetic or malonic ester to give the cyclic isoureides. These were formed at room temperatures when the reaction mixtures were allowed to stand in a desiccator for a few hours. All barbituric acid ethers were confirmed by being converted to barbituric acid.

[†] *Melting points are uncorrected.*

Experimental

I. *Allyl-isourea and Derivatives*

(1) *Allyl-isourea Hydrochloride.* $H_2N\ .\ C(OCH_2CH : CH_2) : \overset{+}{N}H_2\overset{-}{Cl}$*

The salt was obtained as a hygroscopic crystalline solid below room temperature. At room temperature it rapidly melted to an oil. The free base obtained from it by the method described in the introduction was an unstable colourless oil with an odour of allyl alcohol.

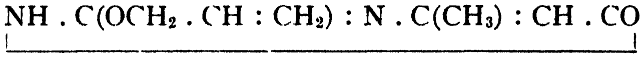
(2) *Allyl-isourea Salicylate*

When the free base in ether solution was mixed with an equivalent of salicylic acid in ether, the salt was obtained in glistening white flakes; m.p., 126° C. Calcd. for $C_{11}H_{14}N_2O_4$: N, 11.76%. Found: N, 11.50, 11.71%.

(3) *Allyl-isourea Benzoate*

White needles; m.p., 148° C. Calcd. for $C_{11}H_{14}N_2O_3$: N, 12.61%. Found: N, 12.56, 12.42%.

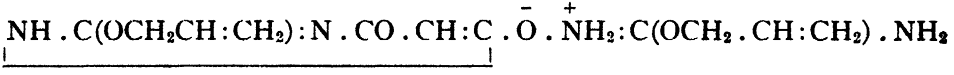
(4) 2-*Alloxy-4-methyl-uracil*



$$\underbrace{NH\ .\ C(OCH_2\ .\ CH : CH_2) : N\ .\ C(CH_3) : CH\ .\ CO}$$

The isoureide was obtained as a white solid when equivalent quantities of the base and ethyl acetoacetate were mixed without a solvent and allowed to stand in a desiccator. It crystallized from benzene in long flat needles; m.p., 164°. Yield, 90%. Calcd. for $C_8H_{10}N_2O_2$: N, 16 86%. Found: N, 16.75, 16 70%.

(5) *Salt of 2-Alloxy-barbituric Acid and Allyl-isourea*



$$\underbrace{NH\ .\ C(OCH_2CH{:}CH_2){:}N\ .\ CO\ .\ CH{:}C}\ .\ \overset{-}{O}\ .\ \overset{+}{N}H_2{:}C(OCH_2\ .\ CH{:}CH_2)\ .\ NH_2$$

The salt was obtained when allyl-isourea was mixed with a slight excess of methyl malonate and the mixture allowed to stand in a desiccator for some hours. It was recrystallized from a mixture of methyl alcohol and ether; m.p., 149 to 150° C. Yield, 60%. Calcd. for $C_{11}H_{16}N_4O_4$: N, 20.90%. Found: N, 21.01, 21.24%.

(6) 2-*Alloxy-barbituric Acid*

The acid was liberated from its salt by the action of dilute hydrochloric acid., It was recrystallized from hot alcohol; m.p., 171°. Yield, quantitative. Calcd. for $C_7H_8N_2O_3$: N, 16.67%. Found: N, 16.35, 16.51%. It was converted to barbituric acid by heating with hydrochloric acid.

II. *Cyclohexyl-isourea and Derivatives*

(1) *Cyclohexyl-isourea Hydrochloride.* $H_2N\ .\ C(OC_6H_{11}) : \overset{+}{N}H_2\overset{-}{Cl}$.

The salt was obtained as a white granular hygroscopic solid. It was recrystallized from ethyl alcohol; m.p., 168°. Yield, 90%. Calcd. for

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**The formulae of isourea salts all indicate the ammonium ion formed by absorption of the proton at the imino-group. In previous papers, the formulae showed the ion formed at the amino-group. The change has been made to conform to the findings of Lecher and his associates on the structure of the guanidinium ion and of thiourea as a switter-ion.*

$C_7H_{14}ON_2 . HCl$: N, 15.72%. Found: N, 15.64%. The free base was obtained as a greasy white solid; m.p., 77 to 78°.

(2) *Cyclohexyl-isourea Salicylate*

Glistening flakes very soluble in alcohol, but rather insoluble in ether, chloroform, or ligroin; m.p., 153°. Calcd. for $C_{14}H_{20}N_2O_4$: N, 10.00%. Found: N, 9.84, 9.73%.

(3) *2-Cyclohexoxy-4-methyl-uracil*

The preparation of this isoureide was similar to that of the allyl compound. It formed white flaky crystals from a mixture of benzene and ligroin. It was very soluble in alcohol; m.p., 110°. Yield, 50%. Calcd. for $C_{11}H_{16}N_2O_2$: N, 13.46%. Found: N, 13.33, 13.25%.

(4) *Salt of 2-Cyclohexoxy-barbituric Acid and Cyclohexyl-isourea*

(See formula of allyl compound for type structure.)

The compound was obtained by crystallization from ethyl alcohol as a fine white powder; m.p., 190° C. Yield, 60%. Calcd. for $C_{17}H_{28}N_4O_4$: N, 15.91%. Found: N, 15.77, 15.82%.

(5) *2-Cyclohexoxy-barbituric Acid*

The acid was liberated from its salt by means of dilute hydrochloric acid, and recrystallized from alcohol. White powder; m.p., 240° C. Yield, 70%. Calcd. for $C_{10}H_{14}N_2O_3$: N, 13.32%. Found: N, 13.13, 13.21%.

III. *Benzyl-isourea and Derivatives*

(1) Benzyl-isourea hydrochloride obtained as a semicrystalline mass was converted into the free base and neutralized with an ether solution of salicylic acid. The salt was recrystallized from alcohol and found to melt at 140° C. as previously recorded by Basterfield and Powell (2).

(2) *2-Benzoxy-4-methyl-uracil*

Equimolecular quantities of the base and ethyl acetoacetate were mixed and allowed to stand over concentrated sulphuric acid for some hours. The solid formed was recrystallized from alcohol. It melted at 153° C. with decomposition. Analysis showed that the compound was not the simple uracil ether as obtained in other cases, but a product involving a second molecule of benzyl-isourea. The nitrogen content found was 16.09, 16.03%, which agrees with the nitrogen calculated for $C_{20}H_{20}N_4O_2$ (16.11%), a compound which could be formed from one molecule of the benzoxy-methyl-uracil and one of benzyl-isourea with elimination of one molecule of water. The substance was decomposed by dilute hydrochloride acid, with the precipitation of the expected uracil; m.p., 160° C. Calcd. for $C_{12}H_{12}N_2O_2$: N, 12.9%. Found: N, 12.6%.

IV. *m-Nitrobenzyl-isourea and Salts*

(1) *m*-Nitrobenzyl-isourea hydrochloride was obtained in small yield as a semisolid mass. The reaction was carried out in ethylene chlorhydrin and the reaction for cyanamide disappeared in seven days.

(2) *m-Nitrobenzyl-isourea Salicylate*

The free base was liberated from the crude hydrochloride into ether, and the solution neutralized with salicylic acid. The salt was precipitated immediately and was recrystallized from alcohol; m.p., 137° C. The yield was only 7% of the theoretical. Calcd. for $C_{15}H_{15}N_3O_6$: N, 12.3%. Found: N, 12.1, 12.1%.

V. *Phenylethyl-isourea and Derivatives*

(1) *Phenylethyl-isourea Salicylate*

The salt formed by the usual procedure was crystallized from alcohol; it melted at 158° C. Calcd. for $C_{16}H_{18}N_2O_4$: N, 9.27%. Found: N, 9.33, 9.24%

(2) 2-*Phenylethoxy-4-methyl-uracil* (?)

The preparation of this compound was similar to that of the benzyl compound. The solid after recrystallization from alcohol melted at 178° C. Yield, about 40%. The product was accidentally lost before an analysis was made.

VI. *β-Hydroxyethyl-isourea Salts*

(1) *β-Hydroxyethyl-isourea Hydrochloride.* $H_2NC(OCH_2 . CH_2OH) : \overset{+}{N}H_2\overset{-}{Cl}$

In the first preparations cyanamide was dissolved in ethylene glycol, and the calculated amount of dry hydrogen chloride passed into solution. When the reaction for cyanamide had disappeared, the excess of glycol was removed by vacuum distillation and the residue was poured into ice cold ether. The white solid obtained was not the expected hydrochloride and yielded no base by the usual procedure. When the procedure was modified by pouring the whole reaction mixture into ether without previous distillation of excess glycol, the precipitated solid yielded a small amount of the expected isourea when suitably treated.

A much better result was obtained by dissolving equimolecular quantities of cyanamide and glycol in ethylene chlorhydrin and treating the solution with the required amount of hydrogen chloride. The reaction mixture was poured into cold ether, and the isourea hydrochloride was precipitated as an oil which solidified at −12° C. At room temperature it formed an oily mush of crystals.

(2) *β-Hydroxyethyl-isourea Salicylate and Benzoate*

The impure hydrochloride was converted to the free base in the usual way, and the ether solution of the latter mixed with an ether solution of salicylic acid. The salt appeared in silky flakes; m.p., 141.5° C. Calcd. for $C_{10}H_{14}N_2O_5$; N, 11.56%. Found: N, 11.32, 11.37%.

The benzoate was obtained in a similar manner, as a mass of fine hair-like crystals; m.p., 134° C. Calcd. for $C_{10}H_{14}N_2O_4$: N, 12.39%. Found: N, 12.25, 12.30%.

VII. *β-Ethoxy-ethyl-isourea Salts and Derivatives*

(1) *β-Ethoxy-ethyl-isourea Hydrochloride.* $H_2N.C(OCH_2CH_2OC_2H_5):\overset{+}{N}H_2\overset{-}{Cl}$.

A mixture of cyanamide and glycol mono-ethyl ether was treated with hydrogen chloride. The reaction for the preparation of this compound was carried out with an excess of the alcohol itself as the solvent. The hydrochloride was obtained as a reddish mush of crystals, which was converted in the usual way to the free base. The latter was a colourless oil, which slowly deposited crystals of high melting point.

(2) *β-Ethoxy-ethyl-isourea Salicylate*

Two grams of the oil dissolved in ether was neutralized with an equivalent of salicylic acid in ether. The salt separated in flaky crystals; m.p., 101° to 102° C. Yield, almost quantitative. Calcd. for $C_{12}H_{18}N_2O_5$: N, 10.40%. Found: N, 10.27, 10.34%.

(3) *2-(β-Ethoxy-ethoxy)-4-methyl-uracil*

The isourea was mixed with its molecular equivalent of ethyl acetoacetate and allowed to stand in a desiccator. The solid obtained was recrystallized from benzene. It gave fine white needles; m.p., 121° C. Yield, about 50%. Calcd. for $C_9H_{14}N_2O_3$: N, 13.08%. Found: N, 13.20, 13.40%.

(4) *Salt of β-Ethoxy-ethyl-isourea and 2-(β-Ethoxy-ethoxy)-barbituric Acid*

The isourea was mixed with one equivalent of methyl malonate and allowed to stand. The solid was recrystallized from alcohol. It gave white granular crystals; m.p., 158° to 159°. Yield, about 50%. Calcd. for $C_{13}H_{24}N_4O_6$: N, 16.92%. Found: N, 16.99, 17.10%.

(5) *2-(β-Ethoxy-ethoxy)-barbituric Acid*

The compound was immediately precipitated when the above salt was treated with dilute hydrochloric acid. It was recrystallized from alcohol; m.p., 138°. Calcd. for $C_8H_{12}N_2O_4$: N, 14.00%. Found: N, 14.10, 14.21%. The substance was converted into barbituric acid by the action of hot hydrochloric acid.

VIII. *β-Amino-ethyl-isourea Salts*

(1) *β-Amino-ethyl-isourea Dihydrochloride.* $NH_2.C(OCH_2CH_2\overset{+}{N}H_3\overset{-}{Cl}):\overset{+}{N}H_2\overset{-}{Cl}$

Equivalent quantities of cyanamide and ethanolamine were dissolved in ethylene chlorhydrin and two molecular equivalents of gaseous hydrogen chloride passed into the solution. The reaction proceeded for several months. When the reaction was complete the mixture was poured into cold ether, whereupon the hydrochloride was precipitated as a light yellow oil which darkened on standing. It was converted at once to the disalicylate.

(2) *Disalicylate.* $NH_2 . C(OCH_2 . CH_2 . \overset{+}{N}H_3 . \overset{-}{O}OC . C_6H_4OH) : \overset{+}{N}H_2\overset{-}{O}OC . C_6H_4OH$

The oil was treated in the usual way, the free base being liberated into ether and neutralized with salicylic acid. The disalicylate was precipitated as white silky flakes; m.p., 141.5°. Calcd. for $C_{17}H_{21}N_3O_7$: N, 11.08%. Found: N, 10.81, 10.87%.

(3) *Dibenzoate.* Prepared as above for the salicylate. The salt was precipitated as a bulky white powder; m.p., 123°. Calcd. for $C_{17}H_{21}N_3O_5$: N, 12.01%. Found: N, 11.91, 11.98%.

IX. *β-Acetoxyethyl-isourea Salts*

(1) Purified ethylene glycol mono-acetate and cyanamide were dissolved in equimolecular proportions in ethylene chlorhydrin. The hydrochloride of the isourea was obtained as colourless oil.

(2) The free base was liberated into ether and was apparently unstable. The ether solution became cloudy from the separation of polymerized decomposition products and was filtered rapidly into ether solutions of salicylic and benzoic acids.

The salicylate, $NH_2 . C(OCH_2CH_2O . COCH_3)\ \overset{+}{N}H_2 . \overset{-}{O}OC . C_6H_4OH$, was obtained as silky white flakes; m.p., 138°. Calcd. for $C_{12}H_{16}N_2O_6$: N, 9.86%. Found: N, 10 11, 10 20%. The benzoate appeared as masses of fine, hair-like needles; m p., 129°. Calcd. for $C_{12}H_{16}N_2O_5$: N, 10.45%. Found: N, 10.65, 10.75%.

X. *Carbethoxy-methyl-isourea Salts*

(1) *Carbethoxy-methyl-isourea Hydrochloride.* $NH_2 . C(OCH_2 . COOC_2H_5) : \overset{+}{N}H_2\overset{-}{C}l$

Ethyl glycollate and cyanamide dissolved in ethylene chlorhydrin and treated with anhydrous hydrogen chloride gave the isourea hydrochloride as a colourless oil.

(2) The free base liberated into moist ether by the action of potash was apparently hydrolyzed with the loss of the ester group since the salts obtained from it were not *carbethoxy* but *carboxy* isourea salts.

Carboxy-methyl-isourea Salicylate. $NH_2 . C(OCH_2 . COOH) : \overset{+}{N}H_2 . \overset{-}{O}OC . C_6H_4OH$

The free base liberated into ether and neutralized with salicylic acid gave a salt, crystallizing in white glistening flakes from alcohol; m.p., 136°. Calcd. for $C_{10}H_{12}N_2O_6$: N, 10.93%. Found: N, 10.87, 10.69%.

Benzoate. This salt was obtained as a fine powder which crystallized from alcohol in silky needles; m.p., 124°. Calcd. for $C_{10}H_{12}N_2O_5$: N, 11.24%. Found: N, 11.33, 11.36%. It was observed that the ether solution of the free base rapidly became cloudy before it could be neutralized with salicylic acid. It was found necessary to filter it quickly into the ether solution of acid.

It was not determined whether the cloudiness was due to a polymerized decomposition product or to the free base itself, which in this case would be an internal salt and not very soluble in ether.

XI. *m-Hydroxyphenyl-isourea Salts*

(1) Cyanamide and resorcinol in equimolecular proportions were dissolved in ethylene chlorhydrin. The reaction was slow and the isourea hydrochloride was obtained as a red oil when the reaction mixture was poured into ether.

(2) *Salicylate.* $H_2N\,.\,C(OC_6H_4OH) : \overset{+}{N}H_2\,.\,\overset{-}{O}OC\,.\,C_6H_4OH$

The free base liberated in the usual way underwent a rapid change in the ether solution and a brown gummy solid separated which was difficult to filter off. Sufficient base was obtained, however, to give, with salicylic acid, a salt crystallizing in silky flakes from a mixture of methyl alcohol and ether; m.p., 138.5° C. Calcd. for $C_{14}H_{14}N_2O_5$ (mono-isourea): N, 9.65%. Found: N, 9.82, 9.95%.

(3) *Benzoate*

Compact crystalline powder from alcohol; m.p., 128° C. Calcd. for $C_{14}H_{14}N_2O_4$; N, 10.22%. Found: N, 9 96%.

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THE ALKALOIDS OF PAPAVERACEOUS PLANTS*

XXIII. *GLAUCIUM FLAVUM* CRANTZ[1]

By Richard H. F. Manske[2]

Abstract

An exhaustive examination of *Glaucium flavum* has revealed the presence of luteanine, isocorydine, aurotensine, and alkaloid F47 (not yet characterized), in addition to the two alkaloids already known to be present, namely, protopine and glaucine.

It is the opinion of the author that the chemical constituents of a plant are as definite indicators of identity as are taxonomic features. Furthermore, since the identity of the chemical constituents is not a matter of personal interpretation, as are the characters of many criteria used by systematic botanists, it seems reasonable to assume that the nature of the chemical constituents may yield important clues not only in pointing to affinities within genera and families, but in defining species limits. The labour involved in isolating and characterizing the alkaloids of all the plants of the Papaveraceae family is admittedly enormous, but, since the purely chemical knowledge thus obtained would in any case justify the effort, the incidental contribution to botanical knowledge can be regarded as a welcome by-product.

The genus *Glaucium* is represented by some 20 species but in many cases the species limits are ill-defined. A variety of one authority may be given specific rank by another or it may be reduced to the vague designation of a form. It seemed therefore of interest to investigate in considerable detail a well known and recognizable species, the identity of which appears to be in no doubt. Such a species is *Glaucium flavum* Crantz (*Gl. luteum* Scop.) from which Probst in 1839 (8) isolated a mixture of alkaloids which was shown by Fischer in 1901 (2) to consist principally of protopine and an alkaloid termed glaucine. Others, notably Gadamer (3), confirmed Fischer's findings, but in spite of the fact that many investigators isolated glaucine from the same source no additional alkaloids have been reported.† If it were a fact that only two alkaloids are elaborated by *Gl. flavum* it might be expected that many other species of *Glaucium* would elaborate only the same pair. Under such circumstances an attempt to elucidate moot points in botanical classification

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**Since the scope of the work on the alkaloids of fumariaceous plants has extended to the entire Papaveraceae family it is deemed expedient to number the papers sequentially from the former and include in the present title the subfamilies Hypecoideae and Papaveroideae. New alkaloids will be numbered serially following those in previous papers.*

†Fischer's claim to have isolated sanguinarine and chelerythrine has not been substantiated and is probably based upon inadequate identification.

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by chemical methods would fail. It was therefore desirable to make a serious attempt to find other alkaloids, and in fact no fewer than four additional ones have been found. The isolation procedure which the author has used repeatedly was applicable in the present case and no difficulty was encountered in the isolation of pure protopine and glaucine. The mother liquor from the latter yielded an appreciable quantity of luteanine, an alkaloid first found in *Corydalis lutea* (7). It was present to the extent of 0.018%, a figure which compares favourably with the protopine content of 0.046%. Two phenolic alkaloids were found in their appropriate fractions, namely, isocorydine (but no corydine) and aurotensine. The fourth alkaloid (F47) appears to be new but owing to the minute amount obtained it could not be adequately characterized. It is proposed to investigate other species of *Glaucium* as well as some named varieties of *Gl. flavum* and it is expected that alkaloid F47 may become available in larger quantities.

The presence of aurotensine (6) calls for comment in that protoberberine alkaloids are not elaborated by most of the genera included in the Papaveroideae. Isocorydine differs from glaucine chiefly in the relative positions occupied by the O-substituents, and the co-presence of the two types has been commented upon in a previous paper (5). Incidentally, it may be mentioned that glaucentrine (6) could not be found although it had been expected that, in view of the large amount of glaucine, it would be found in fair quantity.

Experimental

The material for this investigation was collected on the Suffolk Coast of England by the late Prof. George Barger and his colleague Prof. John Walton of the University of Edinburgh. The author takes great pleasure in expressing his indebtedness to these scientists, a pleasure which is not unmixed with regrets at the untimely passing of Professor Barger.

There was available a total of 28.8 kilos of dried material comprising young and mature plants as well as the roots. It is therefore probable that all alkaloids elaborated by this plant at any stages of its growth were present in the material. At no point in the isolation of the bases was there obtained an alkaloid resembling chelerythrine or sanguinarine, although the final uncrystallized bases from the combined mother liquors weighed less than 0.3 gm. The isolation procedure repeatedly employed by the author has been followed and the same designations of the various fractions are used (4). It was observed that shaking the aqueous acid solution (S) with chloroform yielded a permanent gel. This was avoided by dropping the chloroform in a fine stream into the aqueous solution until most of the glaucine had been removed. Extraction could then be completed by shaking with the chloroform. The following is a summary:—

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,—glaucine, luteanine, alkaloid F47.

EC—Phenolic bases extracted from alkaline solution by means of ether.—isocorydine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—protopine.

BSE and EES—Phenolic bases precipitated by carbon dioxide,—aurotensine.

The other fractions not here listed were either very small or contained traces of the alkaloids already named.

Glaucine, Luteanine, and Alkaloid F47

The crude fraction (BC) was thoroughly washed by decantation and then by kneading in warm water. After thorough air drying it was suspended in several litres of dry ether and the successive decantates were filtered through a layer of charcoal. The combined extract was evaporated to about 700 cc. and seeded with a nucleus of glaucine. The filtrate from the crystalline glaucine was evaporated to 200 cc., whereupon another crop of glaucine crystallized. The yield of not quite pure glaucine at this point was 150 gm.

The ether was removed from the final filtrate and the resinous residue dissolved in 400 cc. of water containing enough oxalic acid to render the solution acidic to Congo red. The filtered solution was repeatedly extracted with ether. (The semisolid extract which remained from the evaporation of the ether was extracted twice with hot dilute hydrochloric acid and the solution basified with ammonia. Ether then extracted a small amount of a base which remained as a resin when the extract was evaporated. This was virtually insoluble in ether and only sparingly soluble in methanol. In contact with a little chloroform-methanol it dissolved and almost immediately crystallized. It was recrystallized from chloroform-methanol and then consisted of colourless fine needles melting not quite sharply at 280° C.* Alkaloid F47 as thus obtained dissolved in sulphuric acid to yield a yellow solution which on heating became first dark and then purple with a brown cast. The yield was somewhat less than 0 1 gm.) The aqueous solution was then basified with ammonia and the liberated bases were extracted with ether. The washed and dried (potassium hydroxide) extract was evaporated to 100 cc. and seeded again with glaucine. The crop of crystals was removed and the bases in the filtrate were recovered and dissolved in dilute hydrochloric acid. The aqueous solution was then extracted with chloroform (this was necessary to eliminate a small amount of protopine which is carried along into the chloroform extract (C), particularly when the latter is rich in alkaloids) and the chloroform extract evaporated. The residue was dissolved in water and the filtered solution again basified with ammonia and extracted with ether. The ether extract was evaporated to a thin syrup and set aside. The crop of crystals which formed in the course of several days was filtered off and washed with ether. It then melted at 177 to 178° C. After recrystallization from methanol-ether it consisted of colourless fine prisms which melted sharply at 183° C. In admixture with a specimen of luteanine from *C. lutea* there was no depression of the melting point and the colour reactions with

**All melting points are corrected.*

sulphuric acid of the alkaloid from both sources were identical and as follows: in the cold a colourless solution which on heating became bluish-olive only near the boiling point of the acid. The latter colour remained on cooling the solution. The optical activity in methanol was $[\alpha]_D^{30°}$ + 205° ($c = 0.4$). Luteanine yields a hydrobromide which can be readily recrystallized from methanol, in which it is only moderately soluble.

The ethereal filtrate from the luteanine contained only a mixture of luteanine and glaucine. The hydroiodide of glaucine is only sparingly soluble in water (1) while that of luteanine is moderately soluble. A dilute acetic acid solution of the bases from the mother liquor was treated with sodium iodide until no more crystalline precipitate was obtained. The precipitate consisted of the hydroiodide of glaucine. The bases in the filtrate were regenerated and the luteanine was crystallized as far as possible. A repetition of the iodide precipitation on the ultimate mother liquor yielded a further small amount of glaucine and a little more luteanine, but no other bases. The total yield of glaucine was 193 gm. (0.67%) and that of luteanine was 5.2 gm. (0.018%).

Protopine

The isolation of protopine in a pure state from fraction (BS) was in this case most conveniently accomplished as follows. The dark amorphous base was dissolved in dilute hydrochloric acid and the filtered solution diluted to about one litre. It was basified with excess ammonia and shaken with several litres of ether. A large volume of the latter is necessary to avoid the crystallization of the protopine in the separatory funnel. The washed solution was rapidly evaporated and the residue heated with a little methanol. The protopine which crystallized at once was filtered off and recrystallized from chloroform-methanol. It melted either alone or in admixture with an authentic specimen at 210° C. The total yield of protopine was 13.5 gm. (0.046%). The final mother liquor contained a small amount of glaucine which was removed by extracting a hydrochloric acid solution of the bases with chloroform. There was ultimately obtained a colourless resinous base weighing about 0.1 gm. which could not be induced to crystallize.

Isocorydine

The fraction (EC) as first obtained was contaminated with a considerable amount of glaucine and luteanine which were removed by reprecipitation with excess potassium hydroxide. The alkaline filtrate was saturated with carbon dioxide and the base extracted with ether. The residue from the ether extract was converted to hydrochloride in methanol and crystallization hastened by adding ethyl acetate and ether. The hydrochloride was recrystallized from methanol–ethyl-acetate and the free base regenerated by means of ammonia and extracted with ether. The extract was evaporated to a thin syrup and treated with hexane until the incipient turbidity just disappeared on mixing. The large colourless crystals thus obtained melted sharply at 184° C., and admixture with a specimen of isocorydine from *Dicentra canadensis* did not lower the melting point. The total yield was not more than 0.1 gm.

(4 p.p.m.). Corydine could not be detected although its sparingly soluble hydrochloride would have made detection facile.

Aurotensine

The fractions (BSE and EES) contained only a small amount of material and were combined. Treatment with hydrogen chloride in methanol readily yielded a sparingly soluble hydrochloride which was filtered off and washed with methanol. Calcd. for $C_{19}H_{21}O_4N.HCl$: OMe, 17.08%. Found: OMe, 16.92%. The hydrochloride was suspended in water, ammonia added, and then shaken with ether. Crystallization took place before all of the ether had been evaporated and was hastened by the addition of a trace of methanol. The base was recrystallized from methanol and obtained in pale pink rectangular plates which melted with gas evolution at 126 to 127° C. In admixture with a specimen of aurotensine from *Corydalis ochotensis* it melted at the same temperature. The colour reactions in sulphuric acid of the base from the two sources were identical. The total yield, including a small amount obtained from fractions (BCE and EEC), was 1.1 gm. (38 p.p.m.).

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TIME OF SET OF SILICA GELS

IV. THE EFFECT OF ALDEHYDES AND SUGARS OVER A pH RANGE[1]

By L. A. Munro[2] and J. A. Pearce[3]

Abstract

The effects of a series of sugars, aldehydes, and other substances on the time of set of silica gels have been investigated over a pH range. Diacetone alcohol, propionaldehyde, rhamnose hydrate, and xylose give curves similar to those previously obtained with the alcohols having a constant and equal effect at pH 7. The hexoses behave as a group while the disaccharides show divergent effects. Propionaldehyde and acetone give very similar curves. The implications of the results are discussed.

Previous investigations (2, 3, 4) have shown a striking regularity in the molar effect of alcohols on the time of set of silica gels. At pH 7 0, mono- and polyhydric alcohols in 0.5 M concentration gave gels having a setting time 106 to 108% of the time of set of the control gel. For alkaline gels the effect of the addition agents became markedly specific.

The present study was undertaken to determine whether a series of aldehydes and sugars showed a regularity of behaviour as addition agents, and also whether at pH 7 0 or some other hydrogen ion concentration a constant effect was obtained.

Experimental

The technique used was the same as that previously described (2, 3, 4). Since the concentration of silica has little influence on the percentage effect on the time of set, a different concentration of silicate was selected for this study to give mixtures setting in a more convenient time-range. This silicate had a specific gravity of 1.0613 and contained 2.87% SiO_2. Twenty-five cubic centimetre portions of this were used in each 50 cc. of gelating mixture.

The best grades of the following addition agents were used in the investigation: acetone, diacetone alcohol*, aldol*, xylose (two sources), rhamnose hydrate (three sources), dextrose (anhydrous; two sources), dextrose hydrate, levulose (three sources), galactose (four sources), mannose (three sources), maltose (two sources), sucrose (commercial), formaldehyde, acetaldehyde, propionaldehyde, *n*-butyraldehyde, isobutryaldehyde, paraformaldehyde, paraldehyde.

Results

The results are tabulated in Table I. The first line gives the pH of the control gels (±0.02 pH units). Line 2 records the volume of standard acetic acid (1.636 N) in the acid mixture (acetic acid + water + addition

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TABLE I

THE EFFECT OF ADDITION AGENTS, PRESENT IN 0.5 *M* CONCENTRATION, ON GELS DIFFERING IN pH

pH	9.50	8.55	7.70	6.70	5.50
Cc. acid	13.0	14 0	14.5	15.0	16.0
t_c, control gel, min.	15.1	7.12	4.67	7.00	92 2
t_A for acetone	27	56	95	119	125
Diacetone alcohol	4	42	86	117	132
Xylose	142	123	113	107	106
Rhamnose hydrate	81	89	96	111	112
Dextrose (anh.)	184	132	118	111	107
Dextrose hydrate	192	138	120	112	105
Levulose	160	137	126	115	112
Galactose	218	153	126	116	111
Mannose	177		123	112	105
Maltose	108	106	103	100	98
Sucrose	167	131	105	96	91
Formaldehyde	90	101	105	106	104
Acetaldehyde	40	57	75	100	110
Propionaldehyde	27	56	93	110	117
n-Butyraldehyde*	8	56	786	343	340
Paraldehyde**	30	70	102	136	143

**Concentration probably not exactly 0.5 M.*

***Concentration 0 5 M/3 to serve as comparison with acetaldehyde.*

agent = 25 cc.). Line 3 shows the time of set of the control gel in minutes for the above pH values. Subsequent lines show the effect of different addition agents when present in 0.5 *M* concentration. This effect is expressed as time of set with addition agent as percentage of the time of set of the control gel ($t_A = x\%$ of t_c). These values are the mean of from two to six determinations made with samples of the reagents from different sources.

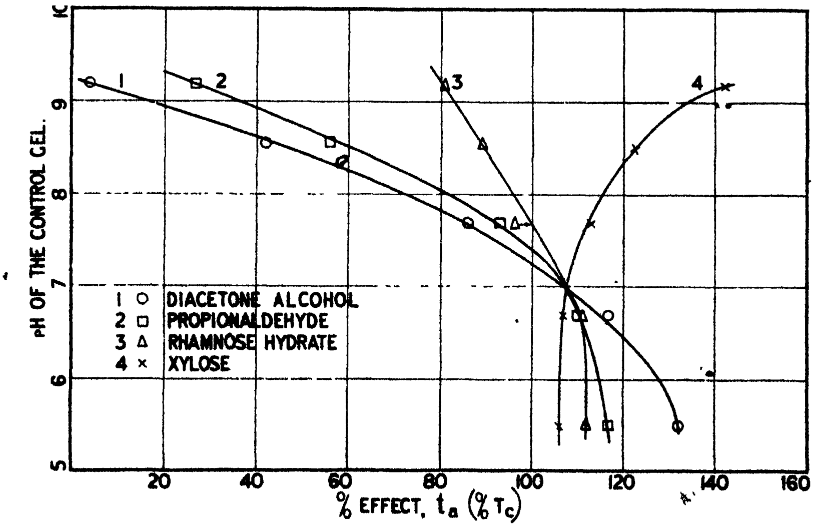

FIG. 1. *The effect of various addition agents (0.5 M/l) expressed as percentage of the time for the control gel.*

Except in the case of one sample of levulose, all samples gave t_a and final pH values agreeing within experimental error.

A plot (Fig. 1) of the data for diacetone alcohol, propionaldehyde, xylose, and rhamnose (hydrate) shows curves very similar to those obtained with the alcohols (4). The diacetone alcohol has a greater effect in alkaline gels than any monohydric alcohol previously studied. The curves for propionaldehyde, rhamnose hydrate, and xylose show a constant effect on the set at pH 7.0, and this effect is almost exactly the same as that previously noted, viz., 106 to 108% of t_c. Xylose simulates a pentahydroxy alcohol in its effect when the medium is alkaline, while the methylpentose behaves more like a mono- or dihydroxy alcohol.

It would be interesting to compare the effects of glucose and methylglucose and other similar compounds.

Hexose Sugars

The results for the hexoses and disaccharides are shown graphically in Fig. 2. It will be seen that the hexose sugars behave as a group, exhibiting little difference in their effects on the time of set. They retard the setting time over the whole pH range studied; in this respect they resemble the polyhydric alcohols. Dextrose hydrate and anhydrous dextrose give virtually the same effects. The retarding effect observed with rhamnose therefore is not due to the fact that the hydrate was used.

The curves for maltose and commercial sucrose show more individuality. Their behaviour is peculiar in that they become accelerators when the medium is acidic. Hurd and Carver (1) obtained a slight lengthening of the time of set for sucrose at pH 5.55. This would bring it more in line with the hexoses. The slight solubility of lactose in the writers' gelating mixture made im-

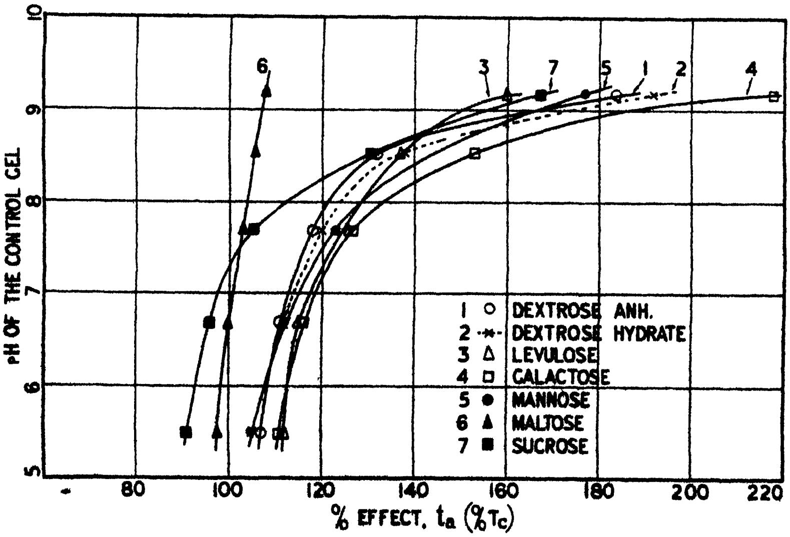

FIG. 2. *The effect of sugars on the time of set.*

possible a satisfactory extrapolation to 0.5 *M* for the curves. It is accordingly omitted.

The Aldehydes

Considerable difficulty was experienced in the study of the aldehydes. It was found that the solubility and other properties changed rapidly, particularly in the cooling thermostat, owing to polymerization. The solubilities of *n*- and isobutyraldehyde, aldol, paraformaldehyde, and paraldehyde are such that results do not represent the effect of 0.5 *M* concentration. However, in so far as could be determined, *n*- and isobutyraldehyde had almost identical effects. These, with paraldehyde and aldol, are accelerators between pH 8.0 and 11.0 and retarders when the medium is acidic. They will have in all cases more pronounced effects than propionaldehyde. Paraformaldehyde was virtually insoluble in the writers' mixtures.

Curves showing the effects of formaldehyde, acetaldehyde, and *n*-propionaldehyde are given in Fig. 3. The curve for acetone is also included. It will be noted that the curve for the ketone is almost identical with that for the aldehyde containing the same number of carbons (methyl groups), except that in the acid region there is a slight divergence. Hurd and Carver's (1) values for acetaldehyde and acetone calculated as percentages of t_c are 112 and 123%, respectively, at pH 5.55. These are in good agreement with the writers' results.

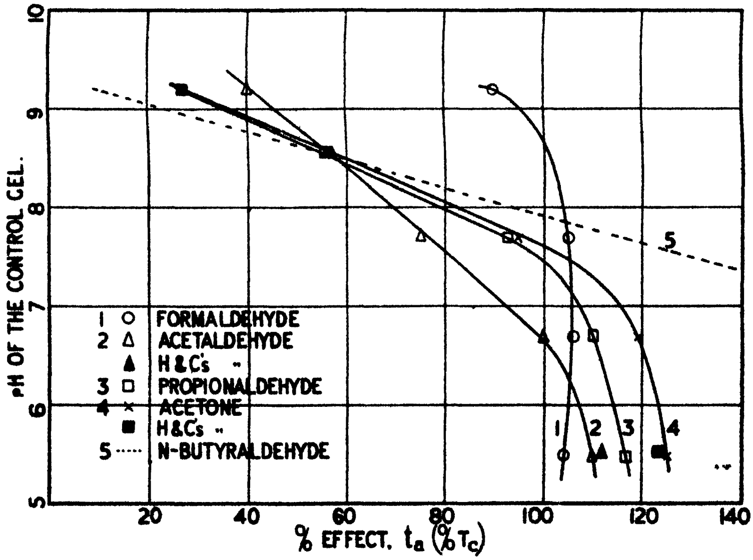

FIG. 3. *The effect of aldehydes and acetone on the time of set. Hurd and Carver's values for acetaldehyde and acetone are shown by solid points.*

Discussion

Recently Tourky (5) has shown by ultra-fine filter dialysis that the maximum amount of aggregation of silicic acid occurs at pH 7.0. There is a more rapid rate of decrease in the amount of silicic acid aggregated as the pH is increased from 7.0 to 11.0 than there is when the pH is decreased from 7.0. The similarity of behaviour of various non-electrolytes as addition agents at pH 7.0 would indicate a molecular effect virtually independent of molecular size or dielectric constant.

It is known that the effect of alkali on the sugars is very complex, involving rearrangement, decomposition, and oxidation. It is therefore improbable that solutions initially containing the same number of molecules of addition agent should give the same effect, but rather that the effect would be similar to that produced by a higher concentration, and the curve would cross the pH 7.0 line at different points. The similarity of the curves for the hexoses is of interest. The divergence of the curves for the aldehydes at pH 7.0 may again be due to a change in the number of molecules present. As with the sugars, the complexity of the system renders difficult any theoretical deductions. The study shows, however, the effect on the time of set obtained when similar molar concentrations of these substances are initially present.

Tourky (5) finds also that there is no aggregation of silica beyond pH 11.0. This is in agreement with the writers' observations (4).

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Errata

Page 53, second paragraph under "Experimental", third line, for "ophiocarpine (F40)" read "ophiocarpine (F39)", and for "alkaloid F39" read "alkaloid F40".

Page 318, third line of abstract, for "glass, wool and celanese" read "glass wool and celanese".

Page 318, third paragraph, first line, for "*k*" read "*K*".